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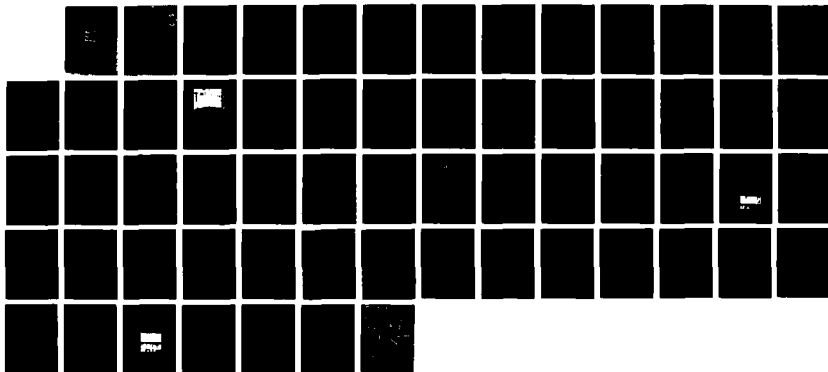
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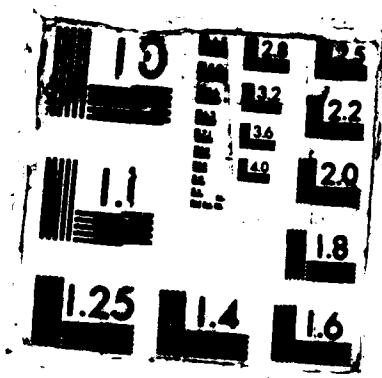
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The objective of this project is to investigate the epitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth technique at low temperatures. Major efforts have been directed to (1) the design and construction of a low pressure reaction chamber and control system, and (2) the laser induced deposition and characterization of epitaxial gallium arsenide films by computer controlled MOCVD. Gallium arsenide films have been deposited by the ArF laser-induced MOCVD over a wide range of process parameters. Device quality homoepitaxial GaAs films with specular mirror smooth surface have been obtained in the substrate temperature range of 425-500°C. The deposited films are p-type with hole concentrations of $(3-4) \times 10^{16}$ to $(1-2) \times 10^{18} \text{ cm}^{-3}$. The carbon content in typical GaAs films is 4×10^{17} to $2 \times 10^{18} \text{ cm}^{-3}$. The hole mobilities are $(150-200) \text{ cm}^2/\text{V-sec}$. Thus, the properties of the homoepitaxial GaAs films by the ArF excimer laser-induced MOCVD are similar to those deposited by conventional MOCVD. The heteroepitaxial growth of GaAs films on single crystalline Ge substrates has also been accomplished by the laser-induced MOCVD.

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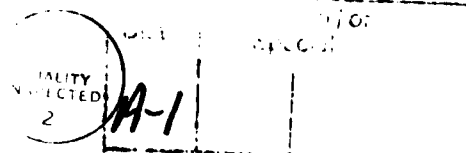
SUMMARY

This is the First Annual Report of a research project "Laser Induced Chemical Vapor Deposition of Gallium Arsenide Films" sponsored by the Free Electron Laser Material Science Program of the office of Naval Research under contract number ONR N00014-86-K-0740. The objective of this project is to investigate the epitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth technique at temperatures considerably below the temperature required in the conventional deposition process.

The approaches used in this program include (a) the use of an excimer laser before the FEL is available, (b) the homo- and hetero-epitaxial growth of GaAs, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ on single crystalline GaAs and Si substrates by using the laser-induced MOCVD process, and (c) the characterization of structural and electronic properties of the deposited films.

Major efforts during this reporting period have been directed to (a) the installation and operation of an excimer laser and a dopant profiler, (b) the determination of optical absorption coefficients of the source materials, (c) the design and construction of a low pressure reaction chamber and the control system, (d) the deposition of homoepitaxial gallium arsenide films by the computer controlled MOCVD system using conventional heating, and (e) the deposition and characterization of gallium arsenide films on single crystalline gallium arsenide and germanium substrates by laser-induced MOCVD.

The deposition of GaAs films have been carried out by the ArF laser-induced MOCVD over a wide range of process parameters. Homoepitaxial GaAs



films with specular mirror smooth surface have been obtained in the substrate temperature range of 425-500°C, considerably below the 650-750°C required for conventional MOCVD. The deposited films are p-type with the hole concentrations in the range of $(3-4) \times 10^{16} \text{ cm}^{-3}$ to $(1-2) \times 10^{18} \text{ cm}^{-3}$. The carbon content in the GaAs films deposited at 500°C is 4×10^{17} to $2 \times 10^{18} \text{ cm}^{-3}$. The hole mobilities are $(150-200) \text{ cm}^2/\text{V-sec}$. Thus, the properties of the homoepitaxial GaAs films by the ArF excimer laser-induced MOCVD are similar to those deposited by the conventional MOCVD technique.

The heteroepitaxial growth of GaAs films on single crystalline Ge substrates has been also carried out by the laser-induced MOCVD. Preliminary results indicate that GaAs films grown on Ge substrates are similar to homoepitaxial GaAs films in properties.

A paper entitled "ArF Excimer Laser-Induced Epitaxial Growth of Gallium Arsenide Films" has been submitted to Applied Physics Letter for publication.

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Section 1.0

INTRODUCTION

This is the First Annual Report of a research project "Laser Induced Chemical Vapor Deposition of Gallium Arsenide Films" sponsored by the Free Electron Laser Material Science Program of the office of Naval Research under contract number ONR N00014-86-K-0740. The objective of this project is to investigate the epitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth technique at temperatures considerably below the temperature required in the conventional deposition process.

III-V compound semiconductors have become increasingly important in electronic devices and circuits. Gallium arsenide (GaAs), indium phosphide (InP), and many III-V ternary and quaternary alloys have unique applications in radiation detectors, solid-state lasers, microwave, electro-optic, and gigabit-rate logic devices. The homo- and hetero-epitaxial growth techniques are essential to provide device-quality III-V compounds and their alloys needed for the majority of these devices.

The three epitaxial technologies in use at present are: vapor phase epitaxy (VPE), liquid phase epitaxy (LPE), and molecular beam epitaxy (MBE). The VPE is currently the dominant epitaxial growth technique used in industry to obtain n- and p-GaAs, InP, and III-V alloys. VPE is a flexible process, and n- and p- layers varying in carrier concentration from mid- 10^{14} to 10^{19} cm^{-3} and thickness from less than one hundredth of a micrometer to 100 micrometers can be grown. The VPE processes can be subdivided into (a) the chloride and (b) the metalorganic chemical vapor deposition (MOCVD) processes. The chloride VPE processes, utilizing

$\text{AsCl}_3\text{-Ga-H}_2$ or HCl-Ga-AsH_3 , are capable of producing epitaxial layers with low carrier concentrations and high electron mobilities. However, the chloride systems have not been successful for the growth of aluminum-containing III-V alloys because of the reactivity of aluminum halides [1]. The epitaxial growth of GaAs by MOCVD using trimethylgallium and arsine in a hydrogen atmosphere was demonstrated in 1969 [2]. Interest in MOCVD technology for the epitaxial growth of III-V compounds has increased considerably since epitaxial layers of microwave device quality were demonstrated [3]. MOCVD has been used for the fabrication of many high performance devices, including lasers, quantum well heterostructures, photocathodes, GaAs low-noise and power FETs, and solar cells [4-8]. Of all the alternative epitaxial techniques, MOCVD has demonstrated the capability to grow the widest variety of III-V materials with excellent doping and thickness control. Monolayer thickness and transition [9,10] are possible. Very low thresholds in $\text{Al}_x\text{Ga}_{1-x}\text{As/GaAs}$ lasers [11] and uniform emission wavelength in $\text{Ga}_{1-x}\text{In}_x\text{P}_{1-y}\text{As}_y$ lasers [12] have also been demonstrated. The process is capable of growing several different III-V alloy systems in the same apparatus, in any sequence, during a single deposition process. For example, abrupt heterojunction structures, such as $\text{GaF}_y\text{As}_{1-y}/\text{Ga}_{1-x}\text{In}_x\text{As}$, has only be prepared by the MOCVD process.

In the conventional MOCVD process, the deposition temperatures are usually in the range of 600-800°C. The advantages of the epitaxial growth of GaAs and other III-V compounds at lower temperatures by the MOCVD technique are well recognized. For example, the contamination and inter-diffusion can be minimized in multilayer device structures, the process-induced defects due to thermal stress can be reduced, and the processing flexibility, such as the epitaxial growth of GaAs on Si, can be increased.

The growth of device quality GaAs on Si substrates can open up many avenues in device fabrication. The major advantage of this technology is the possibility to merge the high electron mobility of GaAs with the high-level integration capabilities of Si. It is anticipated that a new breed of integrated circuits combining Si-based digital circuits with GaAs optoelectronics can be achieved for light-based interconnections. For example, GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ optoelectronic interface units could provide high-data-rate optical link to replace wire interconnects between Si VLSI subsystems. In the near term, the GaAs on Si technology can provide low-cost, less-brittle GaAs wafers since Si wafers have superior mechanical strength. For example, usually as many as half of the bulk GaAs wafers break in most integrated circuit processing lines. GaAs devices would also benefit from the higher thermal conductivity of silicon substrate. Furthermore, GaAs wafers can reach the size of current Si wafers (5 to 8" in diameter). Currently, the bulk GaAs wafers have diameters of only 2 to 3".

The major difficulties involved in obtaining device quality GaAs on Si are the mismatches in lattice parameters (GaAs: 5.654 Å; Si: 5.431 Å) and thermal expansion coefficients (GaAs: $6.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$; Si: $2.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) between GaAs and Si. Because of these mismatches, epitaxial GaAs layers on Si substrates have high dislocation densities, anti-phase domains, and microcracks. The dislocation densities and anti-phase domains can be minimized by using silicon substrates 3° to 4° off the [100] orientation, the germanium interlayer, the superlattice buffer layer, or the combination of low and high processing temperatures. However, the microcracks generated in the epitaxial GaAs layer grown by conventional

MOCVD cannot be eliminated due to the use of high deposition temperatures. Therefore, the epitaxial growth of GaAs on Si at reduced growth temperature with reasonable growth rates is desirable to produce crack-free films.

Several reduced temperature growth techniques are available, such as molecular beam epitaxy (MBE) and plasma-enhanced MOCVD. Although the GaAs film deposited by the MBE technique is of high quality, the MBE technique requires the use of ultrahigh vacuum, and the deposition rate is very low ($\sim 1 \mu\text{m/hr}$) [13]. The epitaxial growth of GaAs by plasma-enhanced MOCVD with growth rate of about $0.1 \mu\text{m/min}$ at $300^\circ - 500^\circ\text{C}$ has been reported [14]; however, this process has not been extensively studied to determine the quality of the deposited films. The use of high power ultraviolet radiation and tunable wavelength FEL offers a novel approach to the preparation of device-quality semiconductor films of controlled electrical and structural properties. The excitation of reaction species to higher electronic states by the FEL will enable the use of considerably lower temperatures for the preparation and crystal growth of semiconductors. The approaches used in this program include (a) the use of an excimer laser before the FEL is available since most of the source materials for the MOCVD of III-V semiconductors absorb radiation in the ultraviolet region, (b) the homo- and hetero-epitaxial growth of GaAs, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ on single crystalline GaAs and Si substrates by using the laser-induced MOCVD process at deposition temperatures considerably below the temperature required in conventional MOCVD, and (c) the characterization of structural and electronic properties of the deposited films in correlation with the deposition parameters.

Major efforts during this reporting period have been directed to (a) the installation and operation of an excimer laser and a dopant profiler, (b) the determination of optical absorption coefficients of metalorganic compounds, (c) the design and construction of a low pressure reaction chamber and the control system, (d) the deposition of homoepitaxial gallium arsenide films by the computer controlled MOCVD system using conventional heating, and (e) the deposition and characterization of gallium arsenide films on single crystalline gallium arsenide and germanium substrates by laser-induced MOCVD. Homoepitaxial growth of gallium arsenide films has been achieved at temperatures as low as 425°C by laser-induced MOCVD. This capability of low temperature epitaxial growth is expected to have wide industrial applications. A paper entitled "ArF Excimer Laser-Induced Epitaxial Growth of Gallium Arsenide Films," submitted for publication in Applied Physics Letter, is attached as Appendix A. The experimental procedures and results are discussed in the following sections.

Section 2.0

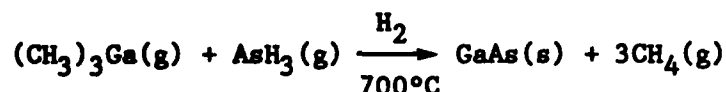
METALORGANIC CHEMICAL VAPOR DEPOSITION (MOCVD)

The MOCVD process was developed in the late sixties [15]. The early work on MOCVD dealt primarily with heteroepitaxial GaAs films on single crystalline insulating substrates, such as sapphire and beryllium oxide [15,16]. During the last ten years, new materials requirements have developed from the increasing interest in the use of certain compound semiconductor devices that employ submicron layers and high quality heterojunctions between two different semiconductor materials. The MOCVD materials technology is well-suited to the fulfillment of these requirements. The use of MOCVD for the growth of thin film III-V compound semiconductors has been widely studied and used for the growth of a number of potentially-important semiconductor devices. The MOCVD process for the growth of III-V semiconductor films is discussed in this section.

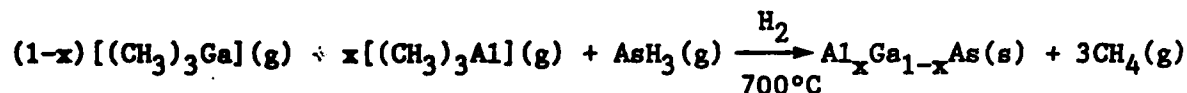
2.1 MOCVD PROCESS

The MOCVD process involves the reaction of gaseous mixtures of one or more hydride and one or more metalorganic compound on the substrate surface. The metalorganics of interest are typically liquids at room temperature with relatively high vapor pressures and can be readily transported into the reactor by bubbling a carrier gas, such as H_2 , through the liquid source. The hydrides of interest are gases at room temperature and are generally used as dilute mixtures in a H_2 matrix. The reaction between the metalorganic compound and the hydride is usually carried out in a H_2 atmosphere in an a gas flow reactor. Deposition temperatures are in the range of 600-800°C. The MOCVD growth of GaAs involves the chemical reaction between trimethylgallium (TMG) (b.p. 55.7°C) and arsine, AsH_3 , in

a hydrogen atmosphere:



Similar reactions are used for the growth of other binary, ternary, and quaternary compound semiconductors. The growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ can be carried out by substituting part of the TMG with trimethylaluminum (TMA):



The composition of the solid solution, x , is directly related to the relative initial partial pressures of TMG and TMA in the vapor phase. This is also true for many quaternary III-V alloys grown by MOCVD, for example, $\text{Ga}_{1-x}\text{Al}_x\text{As}_{1-y}\text{P}_y$. The 'doping' in the grown material can be accomplished by using diethylzinc (DEZ) or bis-cyclopentadienyl magnesium as the p-type dopant and H_2Se or SiH_4 as the n-type dopant.

2.2 MOCVD APPARATUS

A MOCVD reactor consists mainly of the gas handling system and the reaction chamber. A schematic diagram of the MOCVD reactor is shown in Fig. 2-1. The gas handling system includes the source alkyls and hydrides and the instruments necessary to control the gas flows. Hydrogen purified by diffusion through a Pd-Ag alloy is generally used as the carrier gas. The source alkyls are held in temperature controlled baths and electronic mass flow controllers are used to regulate the flow of the carrier gas. The hydrides are gases (usually 10% mixtures in H_2) and the flow rates are also measured by mass flow controllers. Each of the reactants is fed into a common manifold and valving schemes are employed to switch the sources from the reactor manifold to a vent manifold. This allows the intervening

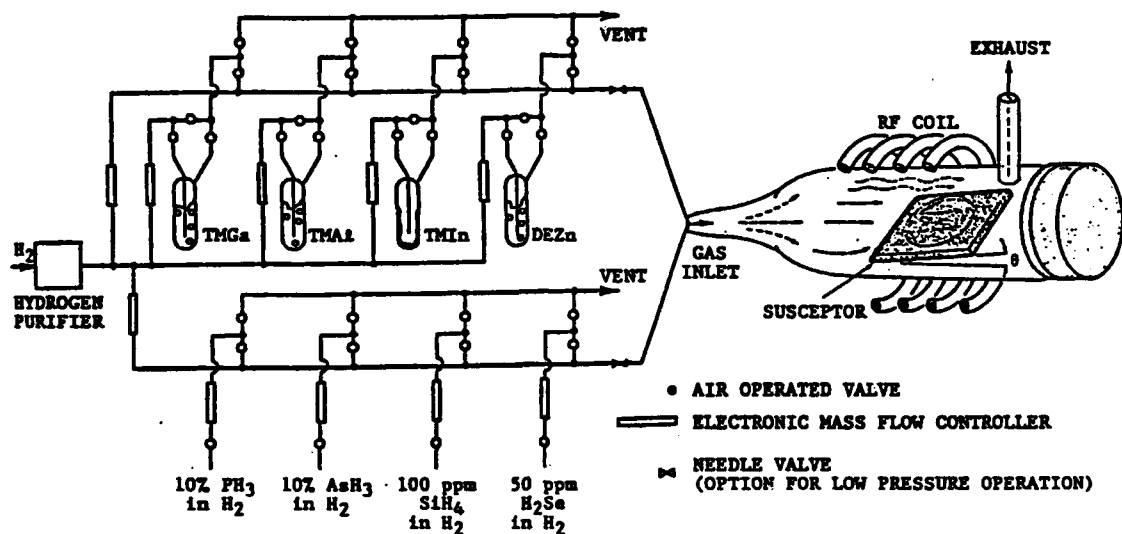


Figure 2-1 Schematic diagram of the MOCVD apparatus.

pipng to fully purge before injection into the reactor, and it also allows injection into the reactor to be terminated without flushing excessive lengths of tubing. The critical valves are automated and interfaced to a computer, as are the flow controllers. A computer controlled MOCVD system has been constructed as shown in Fig. 2-2 and is being used in this project.

In the conventional MOCVD, the substrates are usually placed on a silicon carbide coated graphite susceptor in a fused silica reaction tube, and the susceptor heated externally by an rf generator. This cold-wall reactor avoids undesirable deposition on the wall of the reactor and homogeneous nucleation through reactions in the gas phase. It is essential that the chemical reaction takes place on the heated substrate surface. Volume reaction results in the formation of molecular clusters of random orientations in the space surrounding the substrate, and the deposition of these clusters on the substrate will produce non-adherent deposit. While

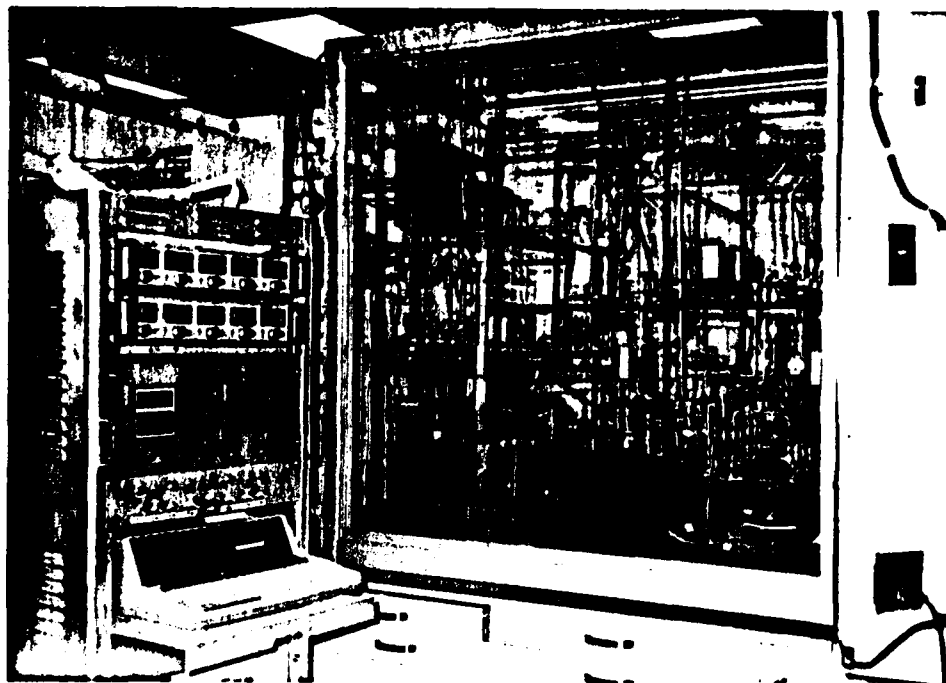


Figure 2-2 A computer controlled MOCVD system.

RF induction is the most commonly used method for heating the susceptor. Radiation from quartz-halogen lamp or resistance heater placed underneath or embedded into the substrate holder has also been used to heat the substrate.

The conventional MOCVD can either be carried out under atmospheric or reduced pressure. The advantage of using reduced pressure is to avoid turbulent flow dynamics and to increase deposition efficiency. A low pressure control system connected to the exhaust of the reaction chamber is essential to maintain a constant pressure in the reaction chamber. Furthermore, a control orifice or valve positioned between the manifold and the low pressure reaction chamber is needed so that the gas handling system is operated at a fixed pressure and is independent of the pressure of the reaction chamber.

2.3 MOCVD PROCESS PARAMETERS

As discussed in Section 2.1, the MOCVD technique can be used for the growth of a large variety of III-V binary, ternary, and quaternary compounds. In this section, the process parameters for the homoepitaxial growth of GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by MOCVD will be discussed.

MOCVD is a simple technique in which the growth rate and composition of the epitaxial layer can be controlled independently and are relatively constant over a wide range of growth temperatures. In the case of GaAs, the growth rate is directly proportional to the group III alkyl partial pressure and nearly constant over the temperature range of 600–850°C under excess AsH_3 partial pressure [17]. In this temperature range, the growth rate is mass-transport limited by the diffusion of TMG through the boundary layer over the substrate surface. The growth rate is independent of the AsH_3 partial pressure in the presence of an excess of AsH_3 ($\text{AsH}_3/\text{TMG} > 1$). However, the electrical properties of unintentionally doped GaAs depend on the AsH_3/TMG molar ratio. The free carrier background doping changes from p to n type as the AsH_3/TMG ratio is increased. A typical plot of the background doping as a function of V/III ratio is shown in Fig. 2-3 [18]. The carbon atom has been identified as the residual acceptor, either from the CH_3 or C_2H_5 associated with the alkyls, or from other organic contaminants in the alkyls [19,20]. The higher hole concentration at reduced AsH_3/TMG ratios is attributed to the increase in As vacancies which enhanced the carbon incorporation on As sites. It has been reported that the background level $N_d - N_a$ increases with the increasing AsH_3/TMG ratio and the growth temperature as shown in Figs. 2-4 and 2-5 [7]. The dominant n-type background impurities are Ge and Si in the metal alkyls, and Zn is the dominant background acceptor in more

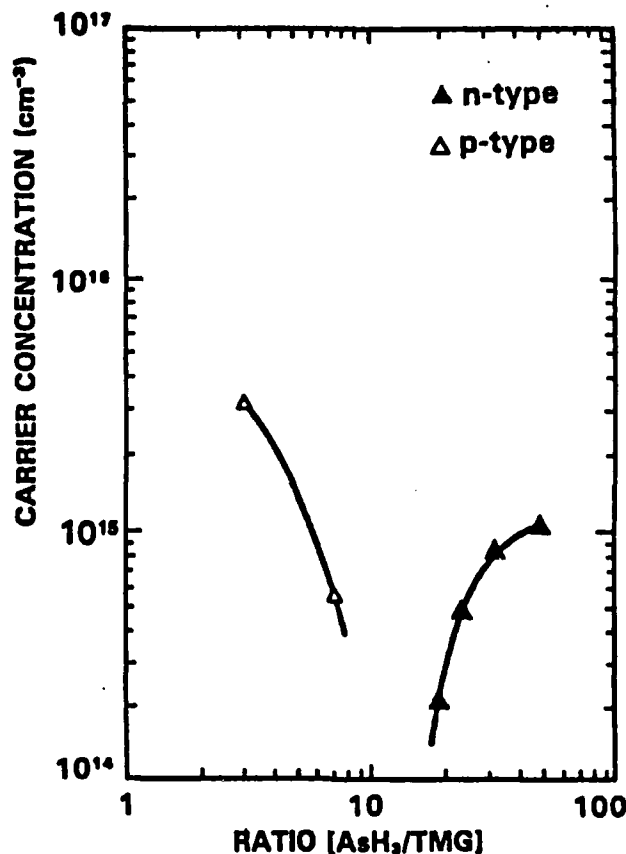


Figure 2-3 Background carrier concentration in GaAs film as a function of AsH₃/TMG ratio.

contaminated GaAs, otherwise C predominates [21]. By further purifying TMG, GaAs with a background doping $n = 3.7 \times 10^{14} \text{ cm}^{-3}$ and electron mobility of $139,000 \text{ cm}^2/\text{V-sec}$ at 77K has been prepared [22,23].

The growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is similar to that of GaAs with the addition of trimethylaluminum (TMA) to TMG in the reaction mixture. There is a close correspondence between the vapor and solid composition of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ over a wide range of substrate temperatures ($600^\circ\text{--}850^\circ\text{C}$) and AsH₃ overpressures. Figure 2-6 shows a plot of composition as a function of the input concentration ratio of $[\text{TMA}]/[\text{TMA} + \text{TMG}]$ [24,25]. There is a tendency that the Al distribution coefficient is slightly higher than unity. The growth rate of the alloy increases with x as shown in Fig. 2-7 [24].

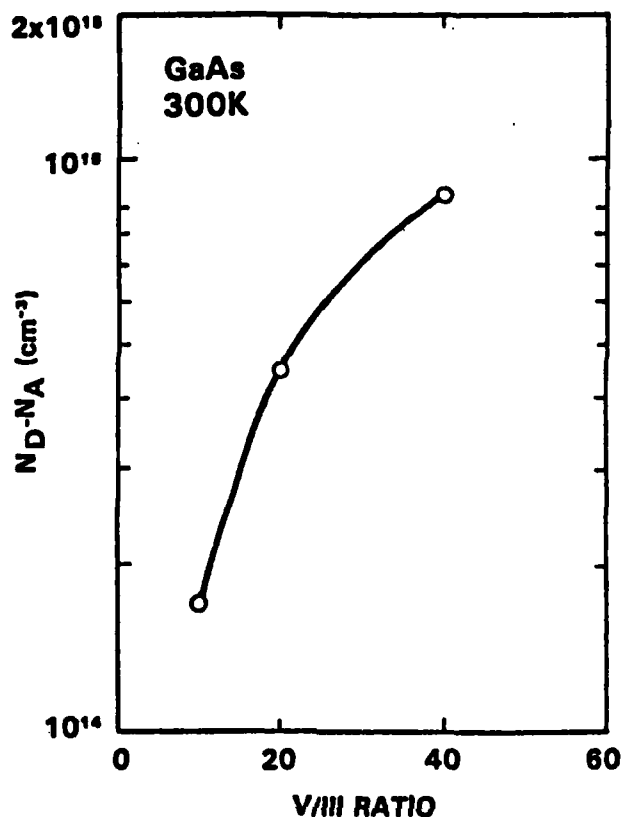


Figure 2-4 Background carrier concentration, $N_D - N_A$, in GaAs as a function of V/III ratio.

At a given alloy composition, the growth rate is proportional to the total alkyl concentration in the reactor and independent of substrate temperature.

The behavior of dopant incorporation can be classified into two categories [26]: (a) all the cracked species incorporate into the growing layer regardless of growth rate (mass transport limited), and (b) the small fraction of incorporated dopant is controlled by a balance between either evaporation back into the gas or attachment to a lattice site (surface kinetic limited). Elements which have a relatively high vapor pressure at growth temperature such as Zn, Cd, S, and Se behave according

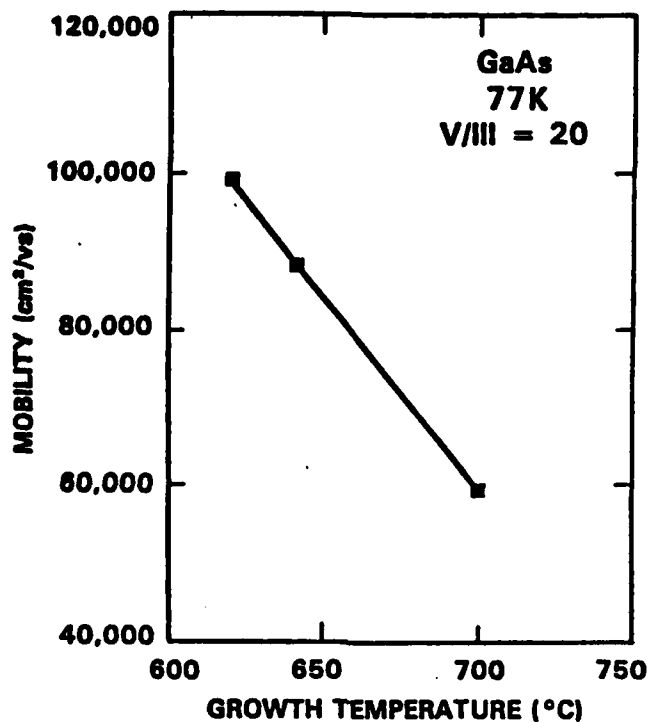


Figure 2-5 Electron mobility (77 K) in GaAs as a function of growth temperature for a V/III ratio of 20.

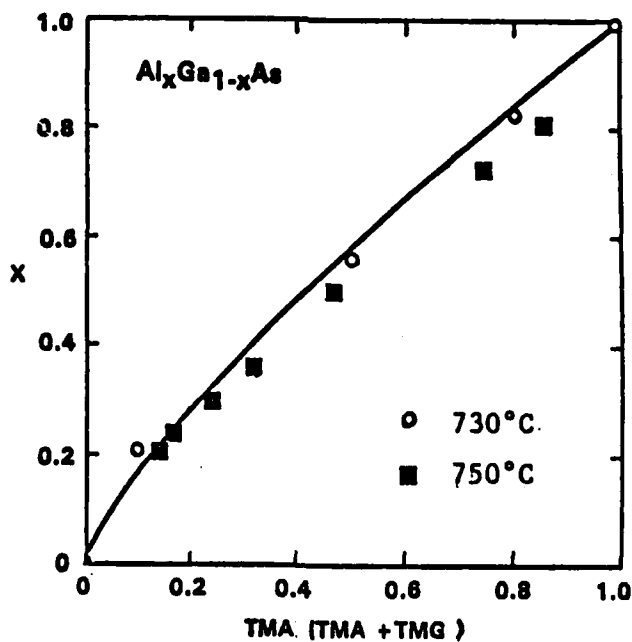


Figure 2-6 Solid composition x of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of gas-phase composition $\text{TMA}/(\text{TMA}+\text{TMG})$.

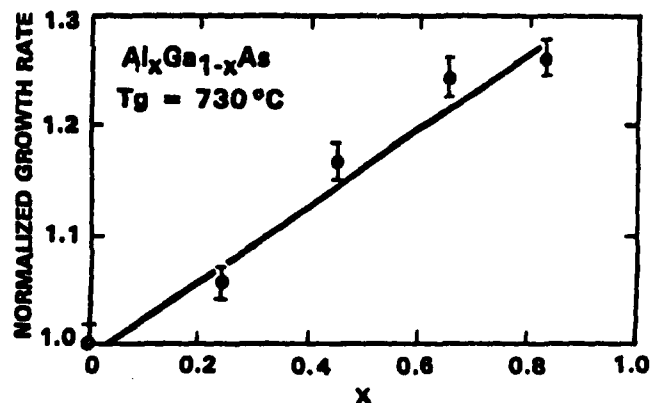


Figure 2-7 Normalized growth rate of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of composition x .

to case (b), whereas those with lower vapor pressures such as Si, Ge, and Sn behave according to case (a).

The two most often used p-type dopants are Zn and Mg. The hole concentrations in GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of the mole fraction of diethylzinc (DEZ) in the gas mixture at a growth temperature of 730°C is shown in Fig. 2-8 [24]. The decrease in doping efficiency with increasing x was attributed to the increase in the acceptor binding energy with higher Al content. There is also a strong dependence of Zn doping on growth temperature as shown in Fig. 2-9 [24]. The source material for Mg doping in MOCVD is biscyclopentadienyl-magnesium (Cp_2Mg). The dependence of hole concentration on Cp_2Mg is proportional to $[\text{Cp}_2\text{Mg mole fraction}]^m$, where $m = 1.78$ [27]. The Mg incorporation is about 10 times more efficient than Zn due to the lower vapor pressure of Mg.

The group IV dopants, Si, Ge, and Sn, always act as donors in GaAs or $\text{Al}_x\text{Ga}_{1-x}\text{As}$ deposited by MOCVD. The electron concentration in GaAs deposited by using SiH_4 or GeH_4 as dopants increases exponentially with growth temperatures as shown in Fig. 2-10. This behavior is opposite to

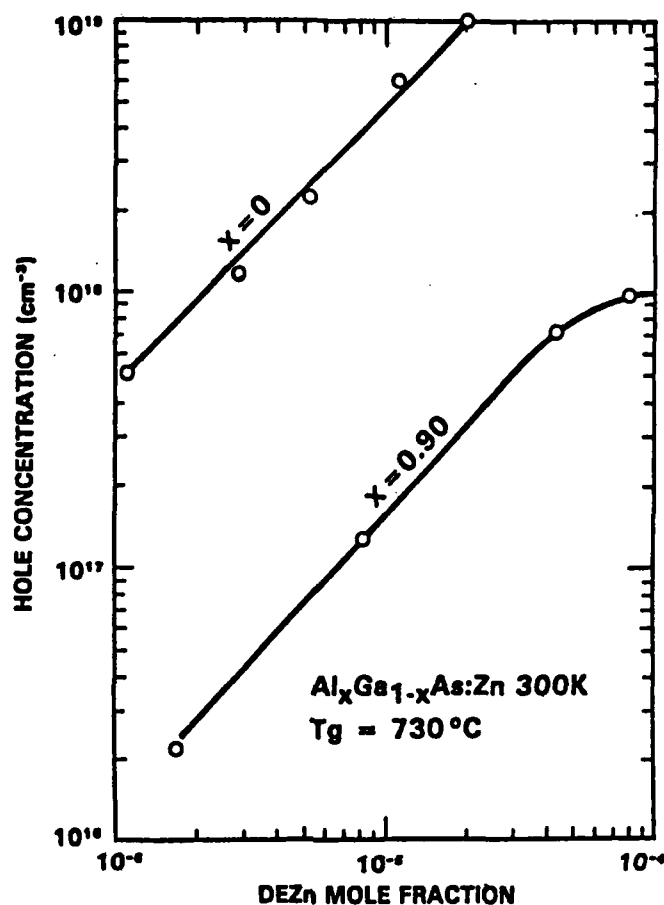


Figure 2-8 Hole concentration in Al_xGa_{1-x}As as a function of diethylzinc (DEZn) mole fraction in the gas phase.

the incorporation of the group II acceptors or group VI donors [28]. The group VI dopants are in the form of dilute mixtures of hydrides of S or Se (H₂S and H₂Se). For S and Se doping, the electron concentrations vary inversely as a function of AsH₃ concentration and growth temperature, but increases with growth rate. As an example, Fig. 2-11 shows a plot of electron concentration as a function of growth temperature for H₂S doping of GaAs [29]. Doping with H₂Se shows the same behavior as that with H₂S. However, both H₂S and H₂Se are polar molecules and tend to adsorb onto and desorb off the reactor walls. This leads to a problem when the dopants are changed abruptly and this problem does not exist with SiH₄ doping.

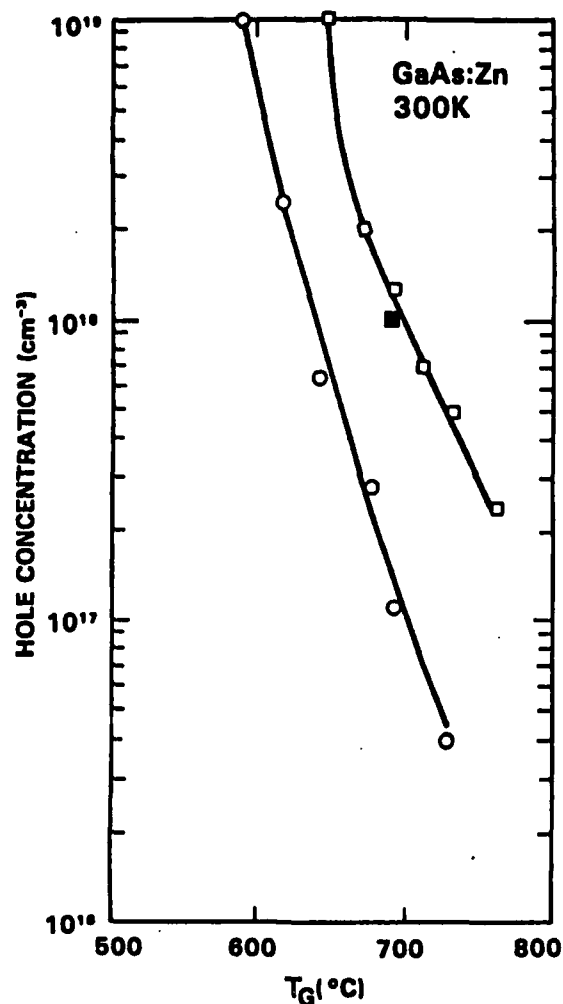


Figure 2-9 Hole concentration in GaAs as a function of growth temperature with Zn-alkyl concentration as a parameter. (a) mole fraction of DMZn = 2×10^{-7} and (b) mole fraction of DEZn = 1.1×10^{-6} .

Furthermore, S reacts with Al at growth temperatures and consequently is not used for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ doping.

2.4 EXPERIMENTAL RESULTS - CONVENTIONAL MOCVD

The epitaxial growth of GaAs films by the conventional MOCVD technique has been carried out using the computer controlled MOCVD system as shown in Fig. 2-2. A horizontal fused silica tube of 55 mm ID was used as

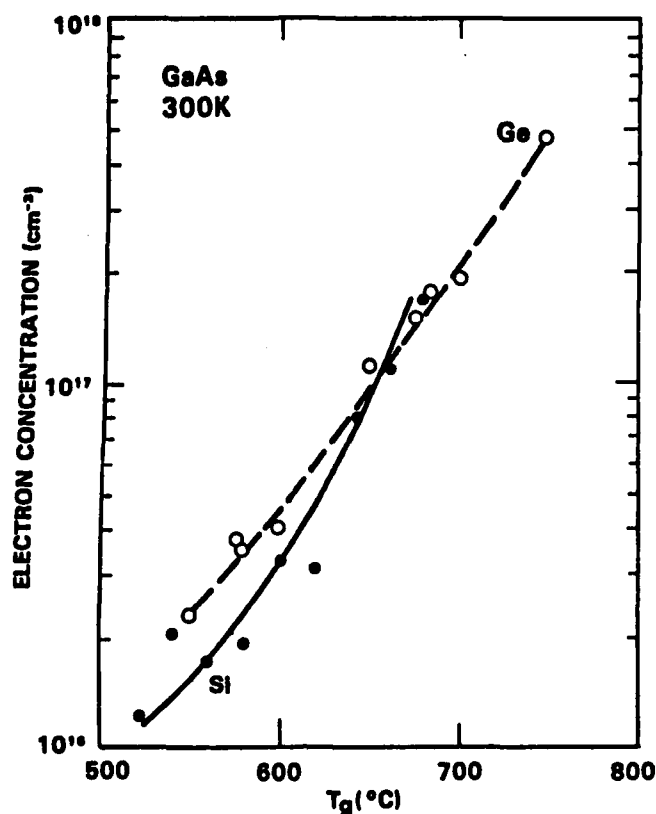


Figure 2-10 Electron concentration in GaAs as a function of growth temperature for Si and Ge doping
 (a) mole fraction of $\text{SiH}_4 = 1 \times 10^{-6}$ and
 (b) mole fraction of $\text{GeH}_4 = 5 \times 10^{-8}$.

the reaction chamber, and the deposition was carried out under atmospheric pressure in a gas flow system. Semi-insulating, single crystalline GaAs wafers of 2° off [100] orientation toward a [110] direction were used as the substrates. The substrates were first etched in 4:1:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution followed by dipping into concentrated HF solution. After rinsing with distilled water, the substrate was placed on a silicon carbide coated graphite susceptor in the fused silica reaction tube. The susceptor was heated externally by an RF generator. A thermocouple inserted into the graphite susceptor was used to monitor the substrate temperature. A 10% mixture of arsine in hydrogen was used as the arsenic source. The TMG

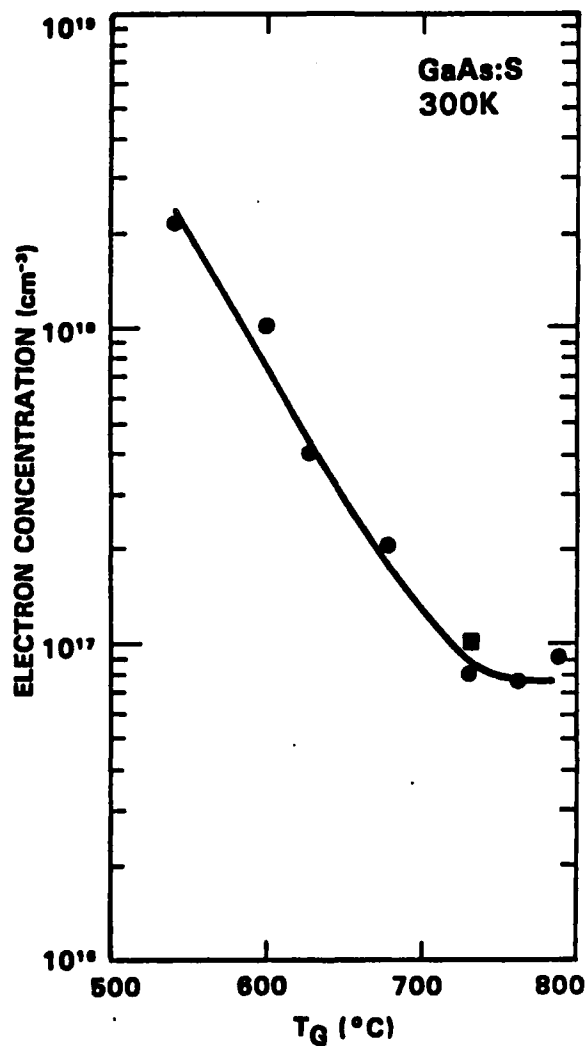


Figure 2-11 Electron concentration in GaAs as a function of growth temperature with H_2S doping.

vapor was introduced into the reaction chamber by bubbling H_2 through the liquid in a stainless steel container, which was held at $0^\circ C$ using a refrigerated constant temperature bath. Hydrogen was used as the carrier gas and the reactant gases were thoroughly mixed before entering the reaction chamber.

Prior to the deposition process, the GaAs substrate was heated to 780°C in hydrogen containing 1% arsine to remove any oxide layer on the substrate surface. Epitaxial GaAs films with good structural perfection have been obtained under various experimental conditions. The deposition temperatures and AsH₃/TMG molar ratios used in these studies are 680°-740°C and 3 to 16, respectively. The mole fraction of TMG in the reaction mixture was fixed at 8.6×10^{-4} . The electrical characteristics of the deposited films were determined by using the Polaron PN 4200 electrochemical carrier concentration profiler and the room temperature Hall measurements. Without intentional doping, the deposited films are n-type when the AsH₃/TMG molar ratios are higher than 10 and are p-type at lower AsH₃/TMG molar ratios. At the AsH₃/TMG molar ratios higher than 10, the electron concentrations in the deposited films increases with increasing growth temperatures. As an example, the net electron concentrations are 9×10^{14} , 2×10^{15} , 2×10^{16} , and $5 \times 10^{16} \text{ cm}^{-3}$ at growth temperatures of 680°, 700°, 720° and 740°C, respectively, using an AsH₃/TMG molar ratio of 16. At the growth temperature of 700°C, the net electron concentration, about $1 \times 10^{15} \text{ cm}^{-3}$, is the lowest at an AsH₃/TMG molar ratio of about 10. The growth rate in the temperature range of 680-740°C is 0.2-0.3 $\mu\text{m}/\text{min}$. A typical electron concentration depth profile of an undoped GaAs film deposited on n⁺-GaAs substrate for 20 minutes at 720°C using an AsH₃/TMG ratio of 16 is shown in Fig. 2-12. The room temperature mobilities of the films deposited at 700°C and 740°C are 6,500 and 5,200 $\text{cm}^2/\text{V}\cdot\text{sec}$, respectively, using the AsH₃/TMG molar ratio of 16. These data are similar to those reported in the literature.

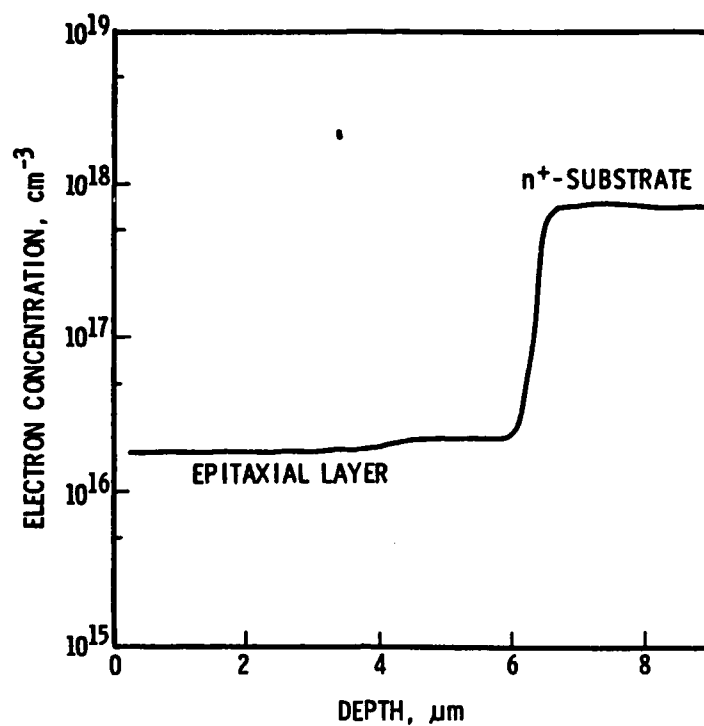


Figure 2-12 Electron concentration depth profile of an undoped GaAs film deposited at 720°C using an AsH₃/TMG ratio of 16.

Section 3.0

SELECTION OF LASER FOR LASER-INDUCED MOCVD

As discussed in Section 1.0, the use of high power ultraviolet radiation and tunable wavelength free-electron laser (FEL) offers a novel approach to the preparation of device quality semiconductor films. The fundamental principles of FELs are now well understood. The gain medium consists of an electron beam moving at speeds close to the speed of light in a magnetic field. The magnetic field is arranged so that the electrons passing through it are deflected alternately left and right. Thus, the electrons execute a wiggly motion through the magnetic field, called the wiggler, and radiate at the frequency of the oscillations. Because of the unique way in which FELs operate, they offer several advantages relative to conventional lasers. They can be tuned to different wavelengths by varying the electron energy. FELs produce excellent optical-beam quality and most importantly, they can be operated at extremely high power. At present, the FELs operate at wavelengths from the millimeter region to the visible part of the spectrum. Experiments using storage rings should produce UV radiation in the next few years. Furthermore, when the better electron-beam quality is achieved, it will be possible to operate FELs at wavelengths as short as 10 nm, in the near-x-ray part of the spectrum. With the improved performance of the laser, there will be a wide variety of applications in the fields of medicine, chemistry, physics, and materials.

Since FEL is not yet available at present time, an excimer laser with laser radiation in the UV region is selected to carry out the objectives

of the current program. The optical absorption characteristics of the source materials for the epitaxial growth of GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ by MOCVD have been studied to determine the wavelength most suitable for the laser-induced MOCVD process. The characteristics of excimer laser and the optical absorption properties of the MOCVD source materials are discussed in this section.

3.1 EXCIMER LASER

Excimer laser are pulsed gas lasers having output at a variety of wavelengths in the ultraviolet region of the spectrum. "Excimer" is a contraction of the term "excited dimer" which refers to a diatomic molecule bound in its electronically excited upper state but repulsive or only weakly bound in its lower ground state. The excimer is formed when the appropriate gas mixture is excited, most commonly in a fast high-voltage electric discharge. For example, in a typical Krypton fluoride (KrF) excimer, the gas mixture contains a buffer gas (such as He or Ne at 3000 Torr), Kr at 60 Torr, and F_2 at a few Torr. The minute concentration of halogens, e.g. F_2 or HCl , is typical of excimer lasers. Excitation of this mixture creates the excited species KrF^* which produces laser radiation at 248.5 nm as a result of the transition to the repulsive ground state.

The major components of an excimer laser is shown schematically in Fig. 3-1 [30]. The electrical discharge is created by transferring the energy stored in the main capacitor, C_1 , to the electrode assembly contained inside the pressure vessel. The electrodes are 50 to 100 cm long, separated by a few centimeters, and oriented parallel to the optical axis. The discharge, or the current flow, is transverse to the optical

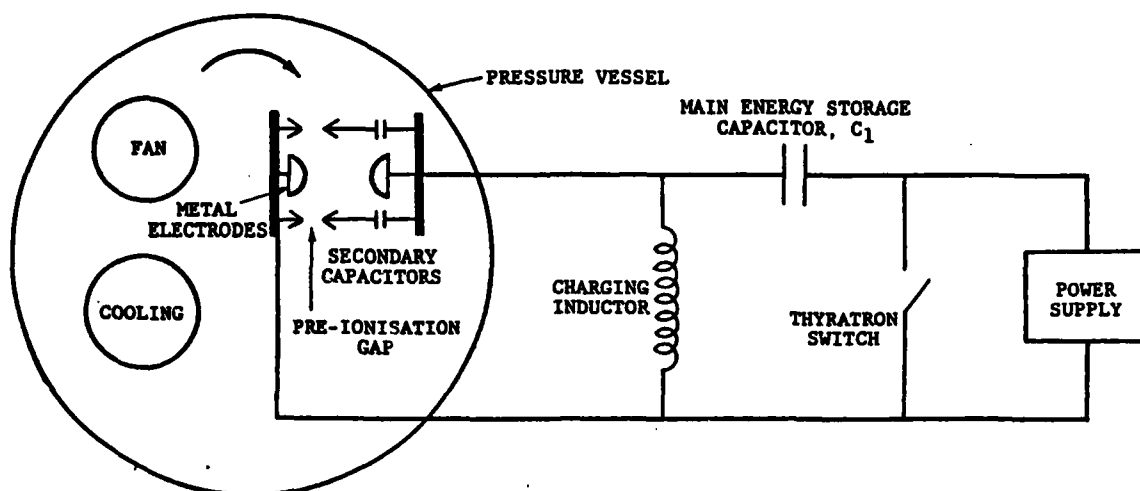


Figure 3-1 Schematic diagram of the major components of an excimer laser.

axis. Through proper design of the electrical circuitry, the excitation of the laser gas occurs in the form of a uniform glow discharge resulting in efficient lasing and long electrode lifetime. The optical resonator is comprised of two mirrors at opposite ends of the electrode assembly. Generally, one mirror is totally reflecting and laser output is extracted through a partially transmitting mirror located at the other end of the electron assembly.

The excimer lasers emit at various wavelengths in the UV spectral region. The specific wavelength is determined by the combination of rare gas and halogen used and the five most common excimers are XeF, XeCl, KrF, KrCl, and ArF. The characteristics of the Lumonics Model HE-460-SM-A excimer laser used in this work are summarized in Table 3-1.

The short wavelength output of the excimer laser is capable of either breaking the chemical bonds or exciting the molecule to its higher electronic states, hence offering a non-thermal means of controlling a reaction. For example, this mechanism can be used to create a desired reactant

Table 3-1. Characteristics of Lumonics Model HE-460-SM-A Excimer Laser

	ArF	KrCl	KrF	XeCl	XeF
Wavelength, nm	193	222	249	308	350
Max. av. power, Watts	25	4.5	45	18	22
Max. pulse energy, mJ	400	70	550	200	275
Pulse rate for max. av. power, Hz	80	80	100	120	100
Pulse duration, ns	10-12	5-8	12-15	8-12	15-20
Beam cross section, mm	8 x 33	6 x 30	10 x 33	6 x 30	9 x 33

species from the source materials such as that required in chemical vapor deposition. Consequently, the deposition reaction can take place at substrate temperatures considerably lower than that required in conventional thermal processing.

3.2 OPTICAL ABSORPTION CHARACTERISTICS

The excimer laser can be operated at five specific wavelengths depending on the combination of rare gas and halogen species as shown in Table 3-1. In order to determine the most optimum wavelength for the laser-induced MOCVD of GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$, the optical absorption characteristics of the source materials in the ultraviolet region must be known. The absorption spectra of TMG, TMA, and a number of other metalorganic compounds have been reported [31,32]. However, the absorption spectra of arsine is not available. The ultraviolet absorption spectra of TMG, TMA, and arsine were determined in this work and were used to compare with the reported data.

The metalorganic compounds, TMG and TMA were of electronic grade manufactured by Alfa Products of Morton Thiokol, Inc, and the 10% arsine in hydrogen was supplied by Phoenix Corporation. The absorption spectra were measured using a Varian Cary 17D Spectrophotometer. For TMG and TMA, pure vapor of the compound in the pressure range of 1-5 Torrs in a sealed fused silica cell was used for the measurement. For arsine, a mixture of 10% in hydrogen with the total pressures in the same range were used. The apparatus used for the preparation of samples for UV spectra measurements is shown schematically in Fig. 3-2. The silica cell is 2.5 cm in diameter and 7.5 cm long with optical windows at both ends. The silica cell is equipped with an inlet tube with a shut-off valve which is used either to evacuate the cell or to fill the cell with desired vapor. Both the silica cell and the TMG or TMA container were evacuated by keeping the container at -80°C . After evacuation, a controlled pressure of the TMG or TMA vapor was introduced into the silica cell which was then sealed and transferred to the spectrophotometer.

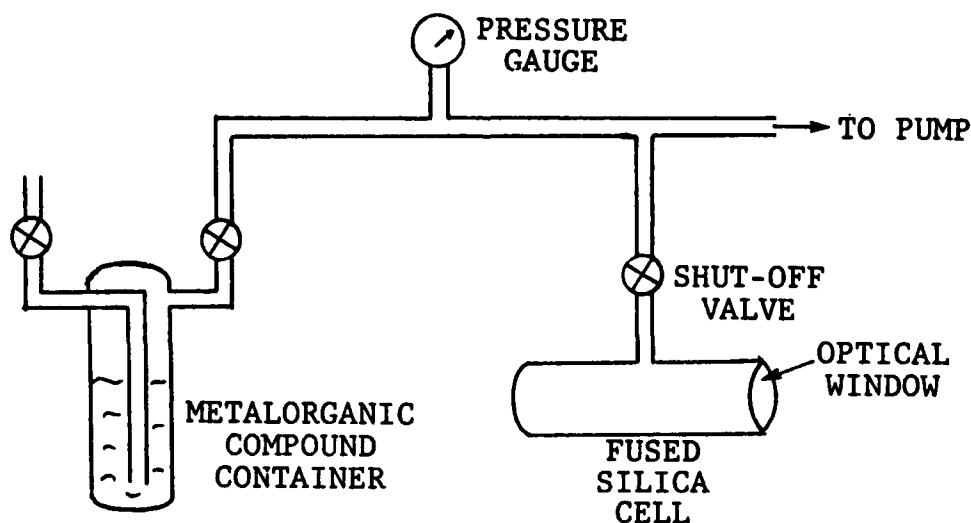


Figure 3-2 Schematic diagram of the apparatus for the preparation of samples for the measurement of UV absorption spectra.

All the light pathways in the spectrophotometer were purged with nitrogen to eliminate the absorption of the UV radiation by oxygen. The absorption spectra of TMG at 1 Torr and TMA at 1.88 Torr are shown in Figs. 3-3 and 3-4, respectively. The maximum absorbance for both compounds occurred at 190 nm. The maximum absorbance shifted to the longer wavelength with broadening of the peak width when the vapor pressure of the organometallic compound is increased. At a fixed wavelength, the absorbance is a linear function of the pressure, as shown in Fig. 3-5 for TMG. The maximum absorbance of 10% AsH₃ in H₂ with a total pressure of 1.5 Torr occurs at a wavelength of 192 nm (Fig. 3-6). Therefore, the ArF excimer laser with 193 nm is best suited for the laser induced MOCVD of GaAs and Al_xGa_{1-x}As.

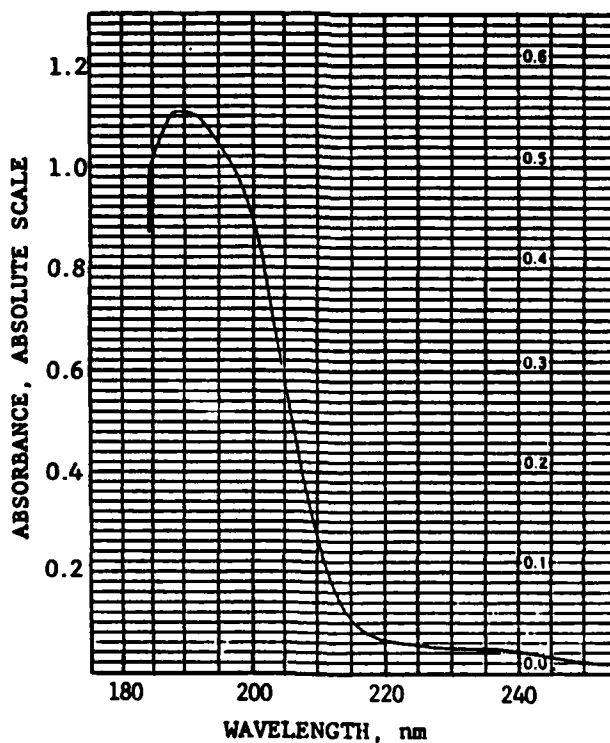


Figure 3-3 Absorption spectrum of TMG.

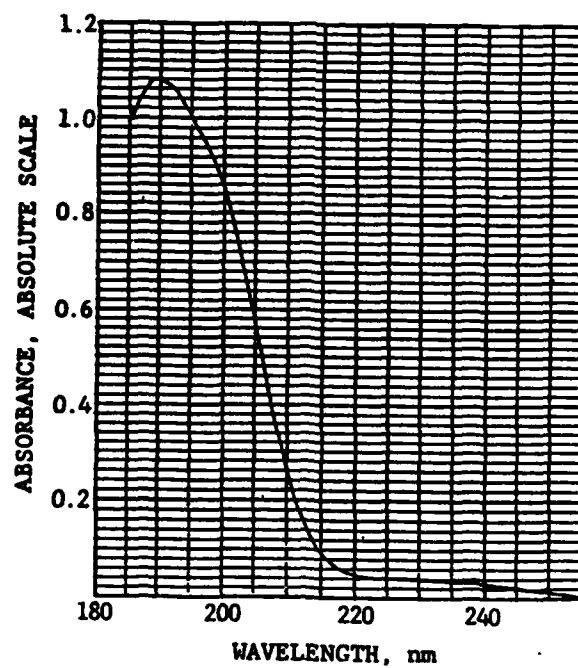


Figure 3-4 Absorption spectrum of TMA.

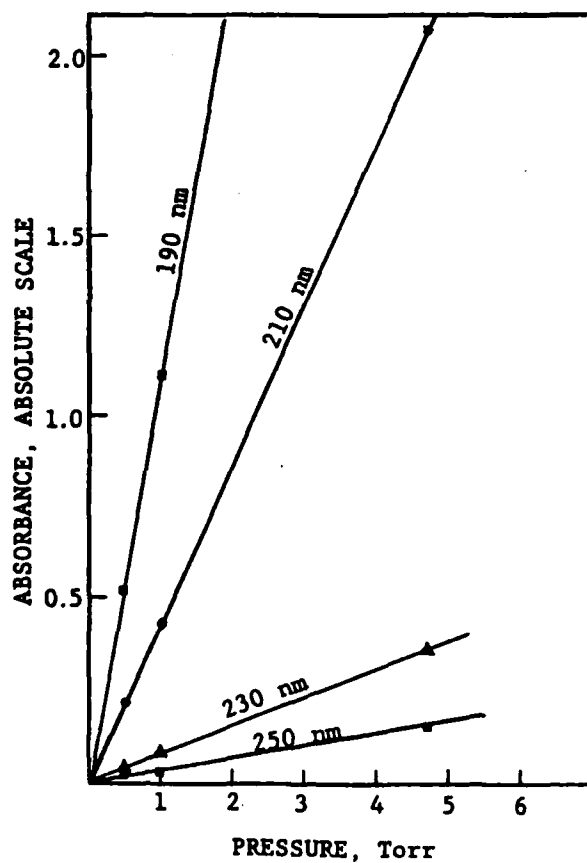


Figure 3-5 Absorbance vs TMA pressure.

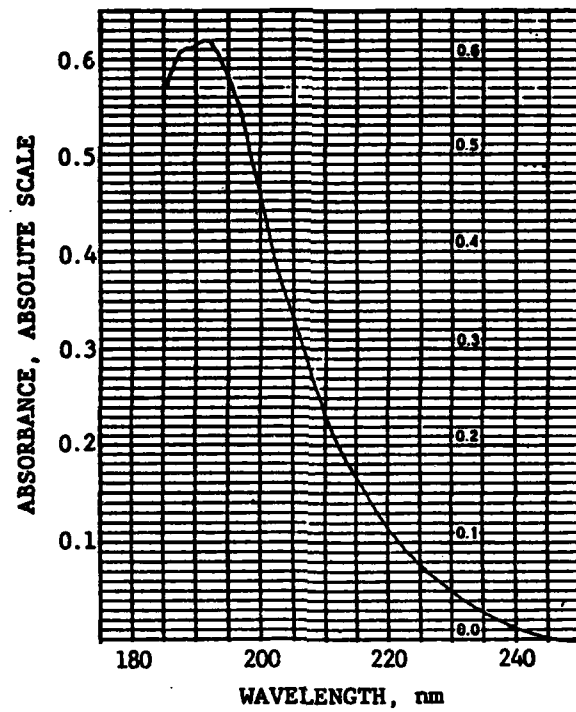


Figure 3-6 Absorption spectrum of 10% AsH₃ in H₂.

Section 4.0

LASER-INDUCED MOCVD

The use of an excimer laser to excite the reaction species to higher electronic states is an attractive approach to the low temperature epitaxial growth of III-V compounds. Homoepitaxial growth of InP films using ArF (193 nm) excimer laser-induced photochemical decomposition of $(\text{CH}_3)_3\text{In}$ and $(\text{CH}_3)_3\text{P}$ at 500°C has been reported [33]. Similar approaches; however, have produced only polycrystalline GaAs films at 400°C using ArF laser stimulated decomposition of $(\text{CH}_3)_3\text{Ga}$ (TMG) and $(\text{CH}_3)_3\text{As}$ [34]. The epitaxial growth of GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ using laser-induced MOCVD is investigated in this program.

A Lumonics Model HE-460-SM-A ArF laser was purchased and put in operation during the initial stage of this program. The characteristics of this laser have been shown in Table 3-1. This laser is capable of operating at constant power under microprocessor control. The laser-induced deposition was carried out under reduced pressure to minimize the gas phase nucleation. The design and construction of the reaction chamber and low pressure control system and the epitaxial growth of GaAs are discussed in this section.

4.1 LOW PRESSURE DEPOSITION SYSTEM

The deposition chamber was made of fused silica with a Suprasil II window, as shown schematically in Fig. 4-1. This chamber was equipped with gas inlet and outlet tubes, purging gas for the window, and thermocouple insert for controlling and monitoring the substrate temperature. The substrate was heated by a quartz halogen lamp and the surface of the substrate was perpendicular to the direction of the laser

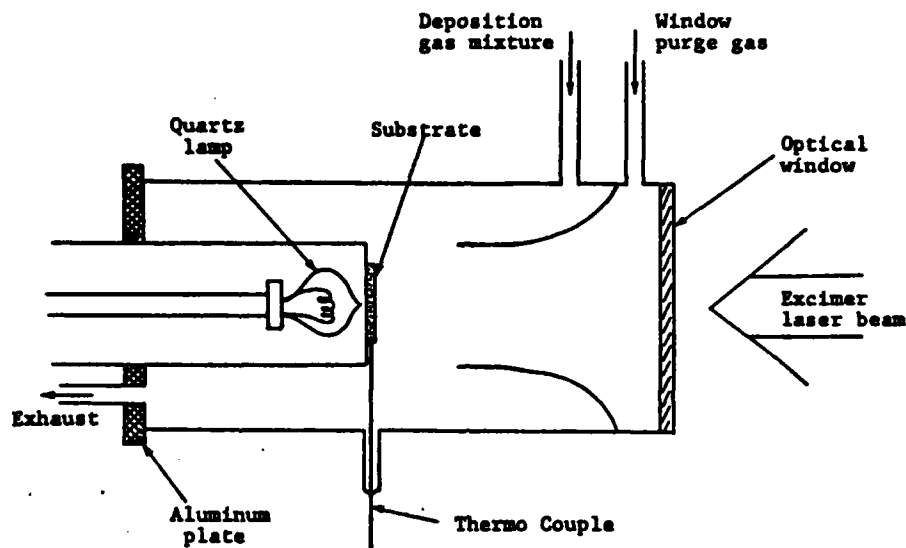


Figure 4-1 Schematic diagram of the reaction chamber.

beam. The low pressure control system, shown in Fig. 4-2, consisted of a microprocessor operated throttle valve, a Baratron gauge, and a vacuum pump. The exhaust gas from the reactor, before entering the throttle valve, was passed through a cracking furnace and a liquid nitrogen trap to ensure the complete decomposition and removal of all unreacted species. The system is capable of controlling the pressure in the reaction chamber down to 1 Torr or less.

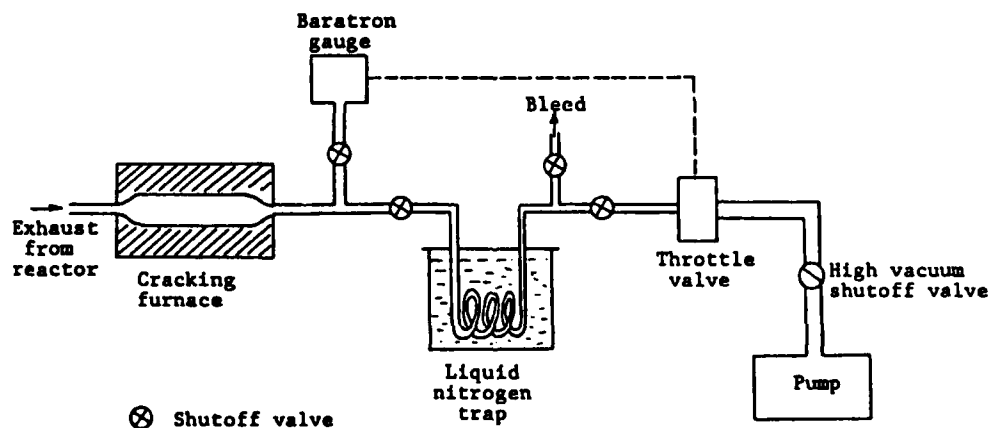


Figure 4-2 Schematic diagram of the low pressure control system.

4.2 DEPOSITION AND CHARACTERIZATION OF HOMOEPITAXIAL GaAs FILMS

The deposition of GaAs films was carried out using the gas handling system described in Section 2.2 by the laser-induced reaction between TMG and AsH₃, and H₂ was used as the diluent and window purging gas. Single crystalline GaAs substrate, after routine cleaning and etching, was placed in the reactor, which was then evacuated. The pressure in the system was maintained at a fixed value, 10-30 Torr, throughout the deposition process. When the substrate reached the deposition temperature, its surface was cleaned in-situ by laser irradiation, and the laser power was adjusted so that the etching caused no damage to the substrate. A number of deposition experiments have been carried out over a wide range of process parameters. Epitaxial GaAs films, on the basis of metallurgical examinations, have been obtained under the deposition conditions of the substrate temperatures of 425-500°C, the laser pulse energy of 80-100 mJ, the laser pulse rate of 60-80 Hz, the mole fraction of TMG of $(1-2) \times 10^{-4}$ and the AsH₃/TMG molar ratio of 4-30. Without laser irradiation, no deposition was observed at temperatures up to 600°C under otherwise the same conditions.

The structural and electrical properties of the deposited films were characterized by using scanning electron microscopy, electrochemical carrier concentration profile, SIMS, and Hall measurements. Specular and mirror smooth films have been deposited at AsH₃/TMG molar ratios of 10 or higher in the temperature range of 425°-500°C. However, the films have hazy appearance when the deposition was carried out at lower AsH₃/TMG molar ratios. The deposition rate was determined by direct measurement of the angle polished and etched cross-sectional surface of the deposited film under SEM and by using the Polaron Model 4200 depth profiler. An

example of a SEM micrograph is shown in Fig. 4-3, where the GaAs film was deposited at 450°C for 10 min using a mole fraction of TMG of 1.6×10^{-4} , AsH₃/TMG molar ratio of 20, laser pulse energy of 95 mJ, and laser pulse rate of 70 Hz. The sample was subsequently angle polished at 5° and etched with the AB etch [35]; the thickness of the epitaxial layer is about 0.5 μm. The epitaxial layer thickness of 0.5 μm was also obtained by using the Polaron depth profiler.

The deposition rate of epitaxial GaAs decreases with decreasing substrate temperature when other process parameters are the same. Figure 4-4 shows a plot of the logarithm of the deposition rate as a function of reciprocal absolute temperature in the temperature range of 425°–500°C. The mole fraction of TMG, AsH₃/TMG molar ratio, laser pulse energy, and laser pulse rate used for these experiments were 1.6×10^{-4} , 20, 95 mJ, and 70 Hz, respectively. The linear relation at substrate

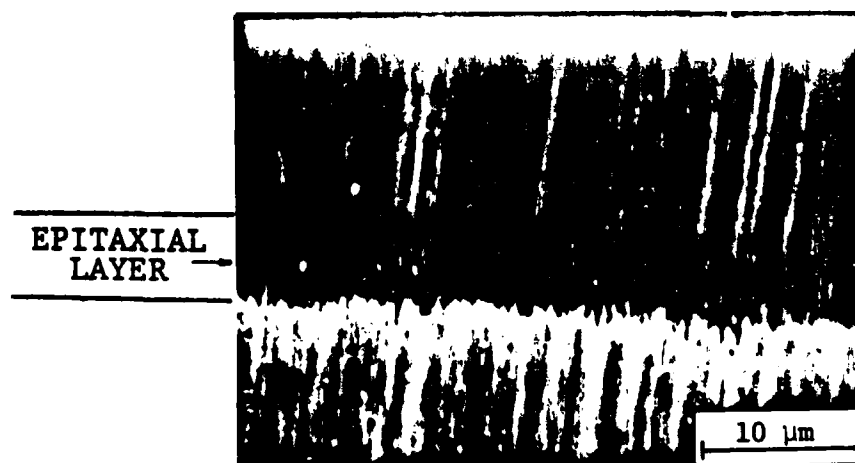


Figure 4-3 SEM of a 5° angle polished and etched cross-sectional surface of a GaAs film deposited at 450°C for 10 min. Deposition conditions: mole fraction of TMG, 1.6×10^{-4} ; AsH₃/TMG molar ratio, 20; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.

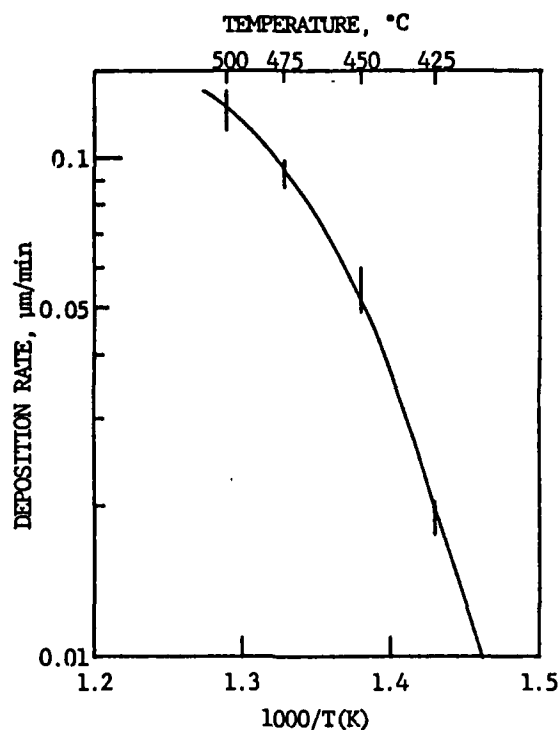


Figure 4-4 The deposition rate of epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 4-3.

temperatures lower than 450°C indicates that the deposition process is controlled by the reaction kinetics at the substrate surface. At higher temperatures, the deposition rate becomes less dependent on the substrate temperature indicating that the mass transport mechanism dominates.

The carrier concentration and mobility of the deposited film have been determined by the van der Pauw's technique. Au-Zn alloy was used as ohmic contacts since all deposited films have p-type conductivity. At a given substrate temperature, the carrier concentration depends strongly on the AsH_3/TMG molar ratio in the reactant mixture. For example, the hole concentration varies from $(1-2) \times 10^{18} \text{ cm}^{-3}$ to $(3-4) \times 10^{16} \text{ cm}^{-3}$ as the AsH_3/TMG molar ratio increased from 4 to 30 at a substrate temperature of

500°C as shown in Fig. 4-5. The carbon content in GaAs films deposited at 500°C was determined by the SIMS technique through the courtesy of Dr. L. Kazmerski of SERI to be 4×10^{17} to $2 \times 10^{18} \text{ cm}^{-3}$. An example of the SIM profile of C and O content in the deposited film is shown in Fig. 4-6. While the carbon concentration is higher in GaAs films deposited at low AsH_3/TMG molar ratios, the carbon content in the films cannot be readily correlated with the carrier concentration. The concentration of oxygen in all films deposited at 500°C was found to be below the detection limit of the SIMS technique, $2 \times 10^{18} \text{ cm}^{-3}$. The hole concentration in GaAs films depends on substrate temperature, and the dependence is more pronounced at low substrate temperatures, as shown in Fig. 4-7. Using a

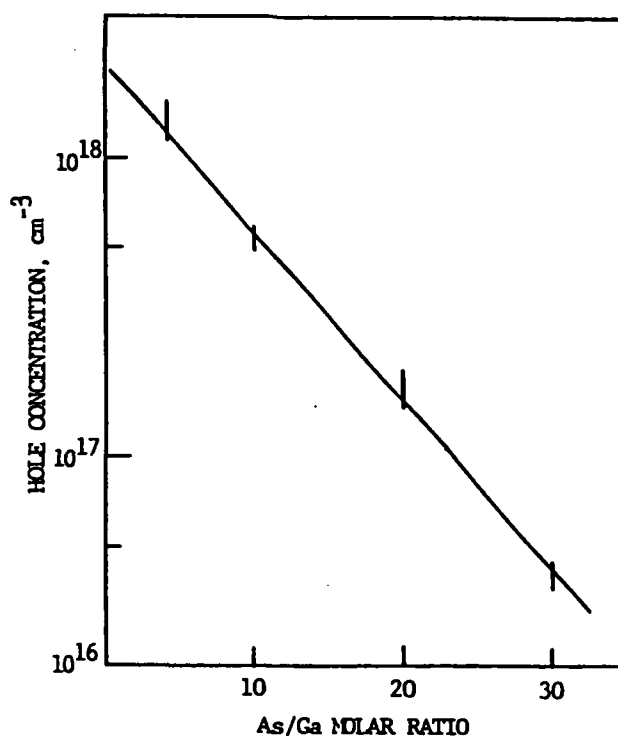


Figure 4-5 The hole concentration in the epitaxial GaAs films deposited at 500°C as function of AsH_3/TMG ratio. Other deposition conditions are the same as those shown in Fig. 4-3.

fixed AsH_3/TMG molar ratio of 20, the hole concentration varies from $5 \times 10^{16} \text{ cm}^{-3}$ at a substrate temperature of 425°C to $(2-3) \times 10^{17} \text{ cm}^{-3}$ at 500°C . This could be due to the higher carbon incorporation at higher deposition temperatures. The hole mobilities are in the range of $(150-200) \text{ cm}^2/\text{V}\cdot\text{sec}$. Thus, the properties of the homoepitaxial GaAs films deposited by the ArF excimer laser-induced MOCVD are very similar to those deposited by the conventional MOCVD technique.

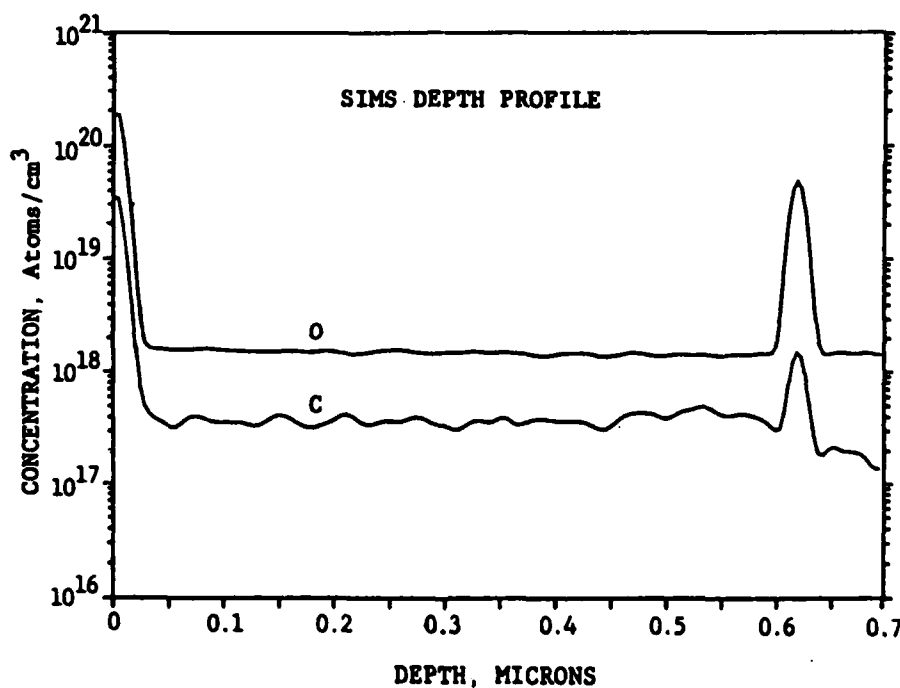


Figure 4-6 SIMS depth profile of C and O content in an epitaxial GaAs film deposited under conditions as those shown in Fig. 4-3.

4.3 DEPOSITION AND CHARACTERIZATION OF HETEROEPITAXIAL GaAs FILMS ON Ge SUBSTRATES

In view of the broad interest of device-quality GaAs films on Si substrates as discussed in Section 1.0, the heteroepitaxial growth of GaAs on Si or on Ge coated Si have been studied by many investigators. The

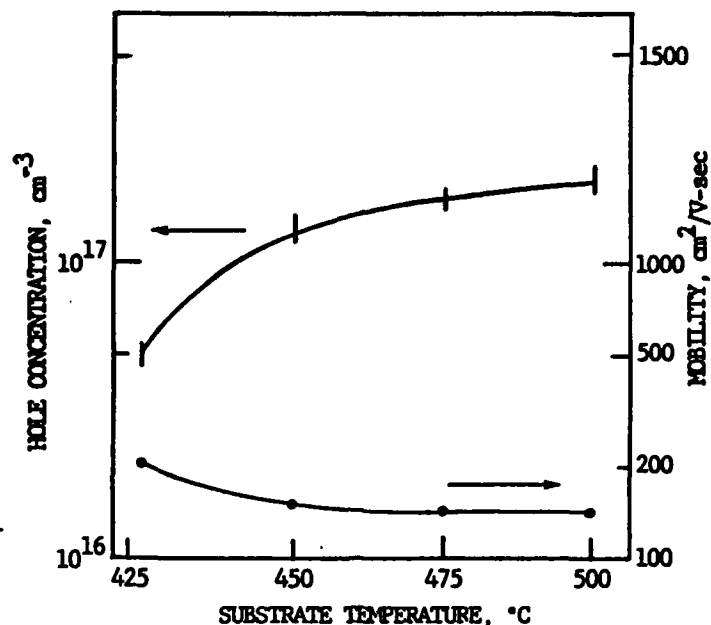


Figure 4-7 The hole condentration and mobility in the epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 4-3.

major technique used for the heteroepitaxial growth are the conventional thermal MOCVD and molecular beam epitaxy (MBE). Device-quality GaAs films have been prepared by thermal CVD using the germanium interlayer [36,37], superlattice buffer layer [38], or the temperature cycling process [39]; however, it is not possible to eliminate the microcracks generated in the GaAs layer due to the high deposition temperatures used in thermal CVD. GaAs devices have been fabricated in various laboratories using Si as the substrates by MBE and MOCVD techniques [40,41,42,43]. The deposition of GaAs by MBE is usually carried out in the temperature range of 550–600°C. The low temperature process can minimize the effect of thermal stress due to the large difference in thermal expansion coefficient between GaAs and Si. However, MBE is not suited for high volume production because of the high equipment cost and the low deposition rate of GaAs. The hetero-

epitaxial growth of GaAs on Ge by laser-induced MOCVD has been carried out and the heteroepitaxial growth of GaAs on Si substrates will be investigated subsequently.

Single crystalline Ge wafers of (100) orientation were used as the substrates. The substrates were cleaned and etched in the CP4 polishing etchant (15 HF, 25 HNO₃, 15 HC₂H₃O₂) for 2 min, followed by thorough rinsing with distilled water. The wafer was then dried with filtered nitrogen and placed in the reaction chamber. Similar to the homoepitaxial growth of GaAs, the Ge substrate surface was also cleaned in-situ by laser irradiation. The deposition was carried out at the substrate temperature of 500°C, the laser pulse energy of 87 mJ, the laser pulse rate of 70 Hz, the mole fraction of TMG of 1.6×10^{-4} , and the AsH₃/TMG molar ratio of 20. Epitaxial GaAs film with specular and mirror smooth surface has been obtained under these conditions. The deposition rate was about 0.1 μm/min and the deposited film was also p-type with a hole concentration of $1.5 \times 10^{17} \text{ cm}^{-3}$ as determined by Polaron electrochemical depth profiler. These values are similar to those obtained by homoepitaxial growth of GaAs under the same deposition conditions.

Section 5.0

REFERENCES

- [1] G. B. Stringfellow, "OMVPE Growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$," J. Crystal Growth, 55, 42 (1981).
- [2] H. M. Manasevit and W. I. Simpson, "Use of Metal Organics in the Preparation of Semiconductor Materials," J. Electrochem. Soc., 120, 135 (1973).
- [3] S. J. Bass, "Device Quality Epitaxial GaAs Grown by the Metal Alkyl Technique," J. Crystal Growth, 31, 172 (1975).
- [4] D. R. Scifres, R. D. Burnham, and W. Streifer, "Mesa Waveguide GaAs/GaAlAs Injection Laser Grown by Metalorganic Chemical Vapor Deposition," Appl. Phys. Lett. 38 915 (1981).
- [5] R. D. Dupuis, P. D. Dapkus, C. W. Garner, C. Y. Su, and W. E. Spicer, "Abrupt $\text{Ga}_{1-x}\text{Al}_x\text{As}$ -GaAs Quantum Well Heterostructures Grown by Metalorganic Chemical Vapor Deposition," Appl. Phys. Lett., 34, 335 (1979).
- [6] J. E. Fouquet, A. E. Siegman, R. D. Burnham, and T. L. Paoli, "Carrier Trapping in Room Temperature, Time Resolved Photoluminescence of a GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ Multiple Quantum Well Structure Grown by Metalorganic Chemical Vapor Deposition," App. Phys. Lett., 46, 374 (1985).
- [7] V. Aebi, S. Bandy, C. Nishimoto, and G. Zdasuik, "Low-Noise Microwave Field-Effect Transistors Using Organometallic GaAs," Appl. Phys. Lett., 44 1056 (1984).
- [8] H. C. Hamaker, C. W. Ford, J. G. Werthen, G. F. Virshup, and N. R. Kaminar, "26% Efficient Magnesium-doped AlGaAs/GaAs Solar Concentrator Cells," Appl. Phys. Lett., 47, (1985).
- [9] J. M. Brown, N. Holonyak, Jr., M. J. Ludowise, W. T. Dietze, and C. R. Lewis, "Monolayer Heterointerface and Thin Layers (~ 10 Å) in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs Superlattice Grown by MOCVD," Electron. Lett., 20, 204 (1984).
- [10] R. J. M. Griffiths, N. G. Chew, A. G. Cullis, and G. C. Joyce, "Structure of GaAs- $\text{Ga}_{1-x}\text{Al}_x\text{As}$ Superlattices Grown by Metalorganic Chemical Vapor Deposition," Electron. Lett., 19, 988 (1983).
- [11] M. D. Camras, N. Holonyak, Jr., M. A. Nixon, R. D. Burnham, W. Streifer, D. R. Scifres, T. L. Paoli, and C. Lindstrom, "Photopumped Low Threshold $\text{Al}_x\text{Ga}_{1-x}\text{As}$ - $\text{Al}_{x'}\text{Ga}_{1-x'}\text{As}$ - $\text{Al}_{x''}\text{Ga}_{1-x''}\text{As}$ ($x \sim 0.85$, $x' \sim 0.3$, $x'' = 0$) Single Quantum Well Lasers," Appl. Phys. Lett., 42, 761 (1983).

- [12] M. Razeghi, M. A. Poisson, M. A. Larivain, and J. P. Duchemin, "Low Pressure Metal-Organic Chemical Vapor Deposition of Indium Phosphide and Related Compounds," J. Electron. Mater., 12, 371 (1983).
- [13] M. Messous and K. E. Singer, "Low-temperature Molecular Beam Epitaxy of Gallium Arsenide," Appl. Phys. Lett., 50, 695 (1987).
- [14] K. P. Pande and A. C. Seabaugh, "Low Temperature Plasma-Enhanced Epitaxy of GaAs," J. Electrochem. Soc., 131, 1357 (1984).
- [15] H. M. Manasevit, "Single Crystal Gallium Arsenide in Insulating Substrates," Appl. Phys. Lett., 12, 156 (1968).
- [16] H. M. Manasevit and W. I. Simpson, "The Use of Metal Organics in the Preparation of Semiconductor Materials. I. Epitaxial Gallium V Compounds," J. Electrochem. Soc., 116, 1725 (1969).
- [17] D. H. Reep and S. K. Ghandi, "Deposition of GaAs Epitaxial Layers by Organometallic Chemical Vapor Deposition," J. Electrochem. Soc., 130, 675 (1983).
- [18] M. O. Watanabe, A. Tanaka, T. Udagawa, T. Nakanisi, and Y. Zohta, "AsH₃ to Ga(CH₃)₃ Molar Ratio Dependence of Dominant Deep Levels in MOCVD GaAs," Jpn. J. Appl. Phys., Pt 1, 22, 923 (1983).
- [19] A. P. Roth, S. Charbonneau, and R. G. Goodchild, "Residual Shallow Acceptors in GaAs Layers Grown by Metal-Organic Vapor Phase Epitaxy," J. Appl. Phys., 54, 5350 (1983).
- [20] N. Kobayashi, T. Fukui, and Horikoshi, "Comparison Between Atmospheric and Reduced Pressure GaAs MOCVD," Jpn. J. Appl. Phys., Pt. 2, 21, L705 (1982).
- [21] K. L. Hess, P. D. Dapkus, H. M. Manasevit, T. S. Low, B. J. Skromme, and G. E. Stillman, "An Analytical Evaluation of Gallium Arsenide Grown with Commercial and Repurified Trimethylgallium," J. Electron. Mater., 11, 1115 (1982).
- [22] P. D. Dapkus, H. M. Manasevit, K. L. Hess, T. S. Low, and G. E. Stillman, "High Purity GaAs Prepared by Trimethyl Ga and AsH₃," J. Cryst. Growth, 55, 10 (1981).
- [23] T. Nakanisi, T. Udagawa, and K. Kamei, "Growth of High Purity Gallium Arsenide Epilayers by MOCVD and Their Application to Microwave MESFET's," J. Cryst. Growth, 55, 255 (1981).
- [24] V. Aebi, C. B. Cooper, III, R. L. Moon, and R. R. Saxena, "Characterization of Organometallic VPE Grown Gallium Arsenide and Aluminum Gallium Arsenide for Solar Cell Applications," J. Cryst. Growth, 55, 517 (1981).

- [25] J. J. Coleman, P. D. Dapkus, D. E. Thompson, and D. R. Clark, "The Growth and Characterization of Metalorganic Chemical Vapor Deposition (MOCVD) Quantum Well Transport Structures," *J. Cryst. Growth*, 55, 207 (1981).
- [26] M. Razeghi and J. P. Duchemin, "Growth and Characterization of Indium Phosphide Using Metalorganic Chemical Vapor Deposition at Reduced Pressure," *J. Cryst. Growth*, 64, 76 (1983).
- [27] C. R. Lewis, W. T. Dietze, and M. J. Ludowise, "The Growth of Magnesium Doped Gallium Arsenide by the OM-VPE Process," *J. Electron. Mater.*, 12, 507 (1983).
- [28] J. P. Duchemin, M. Bonnet, F. Koelsch, and D. Huyghe, "A New Method for Growing GaAs Epilayers by Low Pressure Organometallics," *J. Electrochem. Soc.*, 126, 1134 (1979).
- [29] S. J. Bass and P. E. Oliver, "Controlled Doping of Gallium Arsenide Produced by Vapor Epitaxy, Using Trimethylgallium and Arsine," in *International Symposium on GaAs and Related Compounds*, Edited by L. F. Eastman, St. Louis, 1976, pp. 1-10.
- [30] T. A. Znotins, "Excimer Lasers: An Emerging Technology in Semiconductor Processing," *Solid State Technology*, September 1986, pp. 97-104.
- [31] L. Haigh, "The Vapor-Phase Ultraviolet Spectra of Metalorganic Precursors to III-V Compounds," *J. Mater. Sci.*, 18, 1072 (1983).
- [32] H. H. Gilgen, C. J. Chen, R. Krchnavek, and R. M. Osgood, Jr., "The Physics of Ultraviolet Photodeposition," in *Laser Processing and Diagnostics*, Ed. by D. Bäuerle, Springer, New York, 1984. pp. 225-233.
- [33] V. M. Donnelly, D. Brasen, A. Appelbaum, and M. Geva, "Excimer Laser-Induced Deposition of InP: Crystallographic and Mechanistic Studies," *J. Appl. Phys.* 58, 2022 (1985).
- [34] V. M. Donnelly, V. R. McGrary, A. Appelbaum, D. Brasen, and W. P. Lowe, "ArF Excimer Laser Stimulated Growth of Polycrystalline GaAs Thin Films," *J. Appl. Phys.* 61, 1410 (1987).
- [35] M. S. Abrahams and C. J. Buiocchi, "Etching of Dislocation on the Low-Index Faces of GaAs," *J. Appl. Phys.*, 36, 2855 (1965).
- [36] Shirley S. Chu, T. L. Chu, and H. Firouzi, "Thin-Film GaAs Solar Cells on Germanium-Coated Silicon Substrates by Chemical Vapor Deposition," *Solar Cells*, 20, 237 (1987).
- [37] P. Sheldon, K. M. Jones, R. E. Hayes, B-Y. Tsaur, and J. C. C. Fan, "Growth and Patterning of GaAs/Ge Single Crystal Layers on Si Substrates by Molecular Beam Epitaxy," *App. Phys. Lett.*, 45, 274 (1984).

- [38] R. Fischer, H. Morkoc, D. A. Neumann, H. Zabel, C. Choi, N. Otsuka, M. Longerbone, and L. P. Erickson, "Material Properties of High Quality GaAs Epitaxial Layers Grown on Si Substrates," J. appl. Phys., 60, 1640 (1986).
- [39] Y. Itoh, T. Nishioka, A. Yamamoto, and M. Yamaguchi, "14.5% Conversion Efficiency GaAs Solar Cell Fabricated on Si Substrates," Appl. Phys. Lett., 49, 1614 (1986).
- [40] G. M. Metze, H. K. Choi, and B-Y. Tsaur, "Metal-Semiconductor Field-Effect Transistors Fabricated in GaAs Layers Grown Directly on Si Substrates by Molecular Beam Epitaxy," Appl. Phys. Lett., 45, 1107 (1984).
- [41] M. I. Aksun, H. Morkoc, L. F. Lester, K. H. G. Duh, P. M. Smith, P. C. Chao, M. Longerbone, and L. P. Erickson, "Performance of Quarter-Micron GaAs Metal-Semiconductor Field-Effect Transistors on Si Substrates," Appl. Phys. Lett., 49, 1654 (1986).
- [42] R. M. Fletcher, D. K. Wagner, and J. M. Ballantyne, "GaAs Light-Emitting Diode Fabricated on Ge-Coated Si Substrates," Appl. Phys. Lett., 44, 967 (1984).
- [43] J. P. van der Ziel, R. D. Dupuis, R. A. Logan, R. M. Mikulyak, C. J. Pinzone, and A. Savage, "Low Threshold Pulsed and Continuous Laser Oscillation From AlGaAs/GaAs Double Heterostructures Grown by Metalorganic Vapor Deposition on Si Substrates," Appl. Phys. Lett., 50, 4545 (1987).

APPENDIX A

"ArF Laser-Induced Epitaxial Growth of Gallium Arsenide films"

Submitted to Applied Physics Letters for publication

**ArF Excimer Laser-Induced Epitaxial Growth of
Gallium Arsenide Films**

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Abstract

Epitaxial gallium arsenide films have been deposited on single crystalline GaAs substrates at 425-500°C by ArF excimer laser-induced MOCVD. Using $\text{AsH}_3/(\text{CH}_3)_3\text{Ga}$ molar ratios in the range of 4 to 30, the deposited films are p-type with room temperature carrier concentrations of $10^{16} - 10^{18} \text{ cm}^{-3}$. The films show a specular mirror surface when the $\text{AsH}_3/(\text{CH}_3)_3\text{Ga}$ molar ratio in the reaction mixture exceeds 10. The carrier concentration decreases with increasing $\text{AsH}_3/(\text{CH}_3)_3\text{Ga}$ molar ratio and with decreasing substrate temperature. The carbon concentration in the deposited films, determined by SIMS technique, is in the range of 5×10^{17} to $2 \times 10^{18} \text{ cm}^{-3}$.

The advantages of the epitaxial growth of gallium arsenide and other III-V compounds at low temperatures by the metalorganic chemical vapor deposition (MOCVD) technique is well recognized. For example, the contamination and interdiffusion can be minimized in multilayer device structures, the process-induced defects due to thermal stress can be reduced, and the processing flexibility, such as the epitaxial growth of GaAs on Si, can be increased. Since all group III organic compounds and group V hydrides show strong absorption bands in the ultraviolet,¹ the use of an excimer laser to excite the reaction species to higher electronic states is an attractive approach to the low temperature epitaxial growth of III-V compounds. The homoepitaxial growth of InP films using ArF (193 nm) excimer laser-induced photochemical decomposition of $(\text{CH}_3)_3\text{In}$ and $(\text{CH}_3)_3\text{P}$ at 500°C has been reported.² Similar approaches, however, have produced only polycrystalline GaAs films at 400°C using ArF laser stimulated decomposition of $(\text{CH}_3)_3\text{Ga}$ (TMG) and $(\text{CH}_3)_3\text{As}$.³ In this work, homoepitaxial GaAs films have been deposited at 425°-500°C by ArF excimer laser-induced MOCVD using TMG and AsH_3 . The preliminary results are reported in this letter.

The deposition chamber was made of fused silica with a Suprasil II window, as shown schematically in Fig. 1. This chamber was equipped with gas inlet and outlet tubes, purging gas for the window, and thermocouple insert for controlling and monitoring the substrate temperature. The substrate was heated by a quartz halogen lamp and the surface of the substrate was perpendicular to the direction of the laser beam. The reaction chamber was operated at reduced pressures, and the low pressure control system consisted of a microprocessor operated throttle valve, a Baratron gauge, and a vacuum pump. The exhaust gas from the reactor, before entering the throttle valve, was passed through a cracking furnace and a liquid nitrogen trap to ensure the complete decomposition and removal of all unreacted

species. An Lumonica Model HE-460-SM-A ArF laser (193 nm), operating at constant power under microprocessor control, was used in this work. The beam cross-section area was 8×33 mm.

The deposition of GaAs films was carried out by a computer-controlled MOCVD system using TMG and AsH₃ in a hydrogen atmosphere. Single crystalline GaAs substrate, after routine cleaning and etching, was placed in the reactor, which was then evacuated. The pressure in the system was maintained at a fixed value, 10-30 Torr, throughout the deposition process. When the substrate reached the deposition temperature, its surface was cleaned in-situ by laser irradiation, and the laser power was adjusted so that the etching caused no damage to the substrate. A number of deposition experiments have been carried out over a wide range of process parameters. Epitaxial GaAs films have been obtained, on the basis of metallurgical examinations, under the deposition conditions of the substrate temperature of 425-500°C, the laser pulse energy of 80-100 mJ, the laser pulse rate of 60-80 Hz, and the AsH₃/TMG molar ratio of 4-30. Without laser irradiation, no deposition was observed at temperatures up to 600°C under otherwise the same conditions.

The structural and electrical properties of the deposited films were characterized by using scanning electron microscopy, electrochemical carrier concentration profile, SIMS, and Hall measurements. Specular and mirror smooth films have been deposited at AsH₃/TMG molar ratios of 10 or higher in the temperature range of 425°- 500°C. However, the films have hazy appearance when the deposition was carried out at low AsH₃/TMG molar ratios. The deposition rate was determined by direct measurement of the angle polished and etched cross-sectional surface of the deposited film under SEM and by using the Polaron Model 4200 depth profiler. An example is shown in Fig. 2

where the GaAs film was deposited at 450°C for 10 min. using a mole fraction of TMG of 1.6×10^{-4} , AsH₃/TMG molar ratio of 20, laser pulse energy of 95 mJ, and laser pulse rate of 70 Hz. The sample was subsequently angle polished at 5° and etched with the AB etch;⁴ the thickness of the epitaxial layer is about 0.5 μm. The epitaxial layer thickness of 0.5 μm was also obtained by using the Polaron depth profiler.

The deposition rate of epitaxial GaAs decreases with decreasing substrate temperature when other process parameters are the same. Figure 3 shows a plot of the logarithm of the deposition rate as a function of reciprocal absolute temperature in the temperature range of 425° - 500°C. The mole fraction of TMG, AsH₃/TMG molar ratio, laser pulse energy, and laser pulse rate used for these experiments were 1.6×10^{-4} , 20, 95 mJ, and 70 Hz, respectively. The linear relation at substrate temperatures lower than 450°C, indicates that the deposition process is controlled by the reaction kinetics at the substrate surface. At higher temperatures, the deposition rate becomes more independent on the substrate temperature indicating that the mass transport mechanism dominates.

The carrier concentration and mobility of the deposited film have been determined by the van der Pauw's technique. Au-Zn alloy was used as ohmic contacts since all deposited films have p-type conductivity. At a given substrate temperature, the carrier concentration depends strongly on the AsH₃/TMG molar ratio in the reactant mixture. For example, the hole concentration varies from $(1-2) \times 10^{18} \text{ cm}^{-3}$ to $(3-4) \times 10^{16} \text{ cm}^{-3}$ as the AsH₃/TMG molar ratio increased from 4 to 30 at a substrate temperature of 500°C, as shown in Fig. 4. The carbon content in GaAs films deposited at 500°C was determined by the SIMS technique to be 4×10^{17} to $2 \times 10^{18} \text{ cm}^{-3}$. While the carbon concentration is higher in GaAs films deposited at low AsH₃/TMG molar ratios, the carbon content in the films cannot be readily correlated

with the carrier concentration. The concentration of oxygen in all films deposited at 500°C was found to be below the detection limit of the SIMS technique, $2 \times 10^{18} \text{ cm}^{-3}$. The hole concentration in GaAs films depends on substrate temperature, and the dependence is more pronounced at low substrate temperatures, as shown in Fig. 5. Using a fixed AsH_3/TMG molar ratio of 20, the hole concentration varies from $5 \times 10^{16} \text{ cm}^{-3}$ at a substrate temperature of 425°C to $(2-3) \times 10^{17} \text{ cm}^{-3}$ at 500°C. This could be due to the higher carbon incorporation at higher deposition temperatures. The hole mobilities are in the range of $(150-200) \text{ cm}^2/\text{V-sec}$. Thus, the properties of the homoepitaxial GaAs films deposited by the ArF excimer laser-induced MOCVD are very similar to those deposited by the conventional MOCVD technique.

In summary, good quality homoepitaxial GaAs films have been deposited for the first time by ArF excimer laser induced MOCVD under a range of experimental conditions. The ability of achieving homoepitaxial growth of GaAs at temperature as low as 425°C will have a wide range of applications.

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References

- ¹ J. Haigh, J. Materials Science, 18, 1072 (1983).
- ² V. M. Donnelly, D. Brasen, A. Appelbaum, and M. Geva, J. Appl. Phys. 58, 2022 (1985).
- ³ V. M. Donnelly, V. R. McGrary, A. Appelbaum, D. Brasen, and W. P. Lowe, J. Appl. Phys. 61, 1410 (1987).
- ⁴ M. S. Abrahams and C. J. Buiochi, J. Appl. Phys., 36, 2855 (1965).

Figure Captions

- Figure 1. Schematic diagram of the deposition reaction chamber.
- Figure 2. Scanning electron micrograph of an angle polished and etched cross-sectional surface of a GaAs film deposited at 450°C for 10 mins. The deposition conditions: mole fraction of TMG, 1.6×10^{-4} ; AsH₃/TMG molar ratio, 20; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.
- Figure 3. The deposition rate of epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 2.
- Figure 4. The hole concentration in the epitaxial GaAs films as a function of AsH₃/TMG molar ratio. The depositions conditions: deposition temperature, 500°C; mole fraction of TMG, 1.6×10^{-4} ; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.
- Figure 5. The hole concentration and mobility in the epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 2.

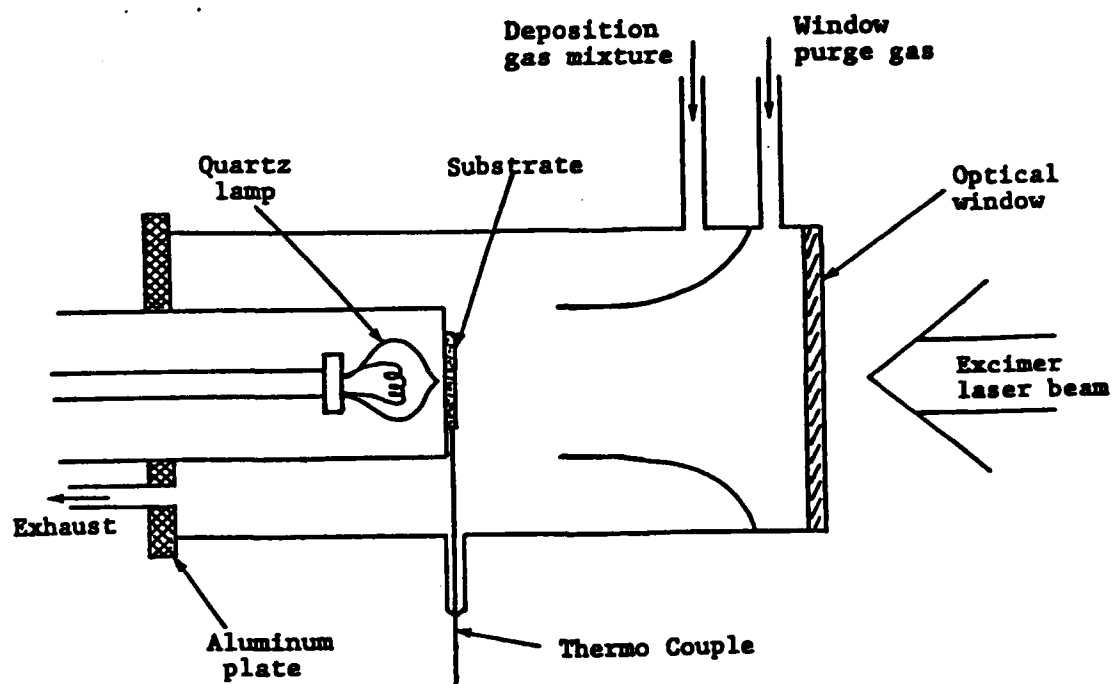


Figure 1. Schematic diagram of the deposition reaction chamber.

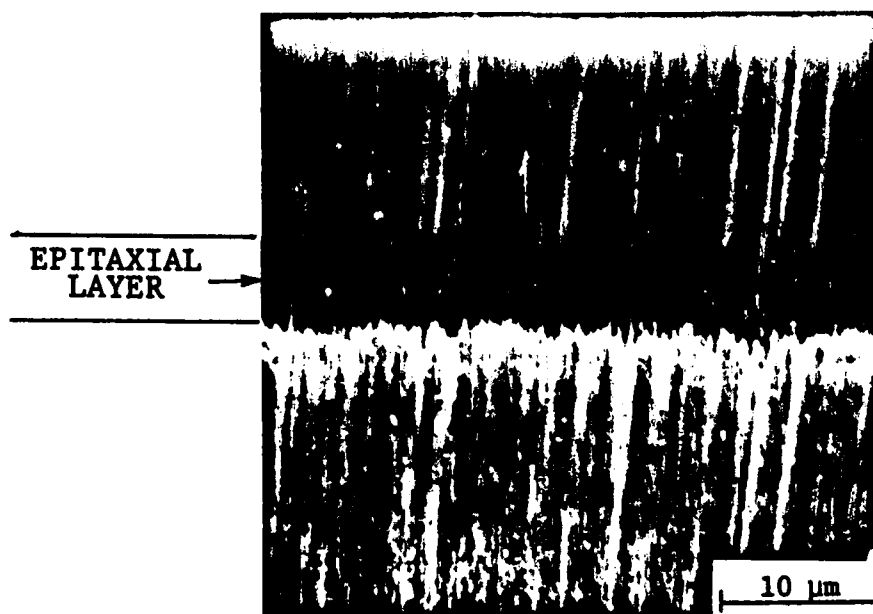


Figure 2. Scanning electron micrograph of an angle polished and etched cross-sectional surface of a GaAs film deposited at 450°C for 10 mins. The deposition conditions: mole fraction of TMG, 1.6×10^{-4} ; AsH_3 /TMG molar ratio, 20; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.

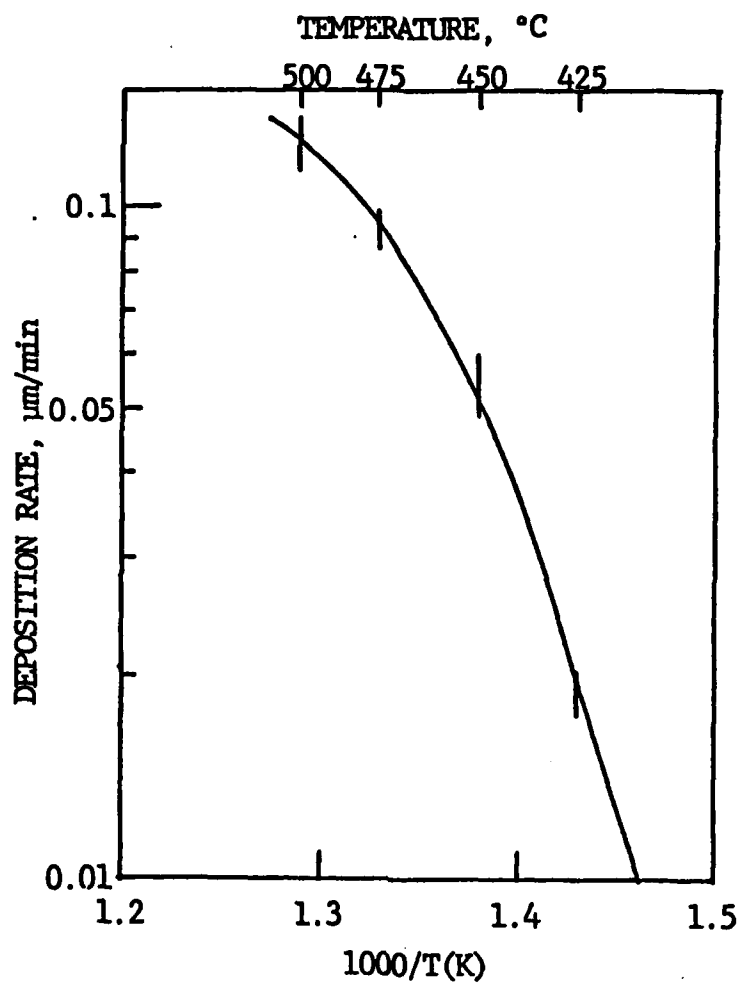


Figure 3. The deposition rate of epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 2.

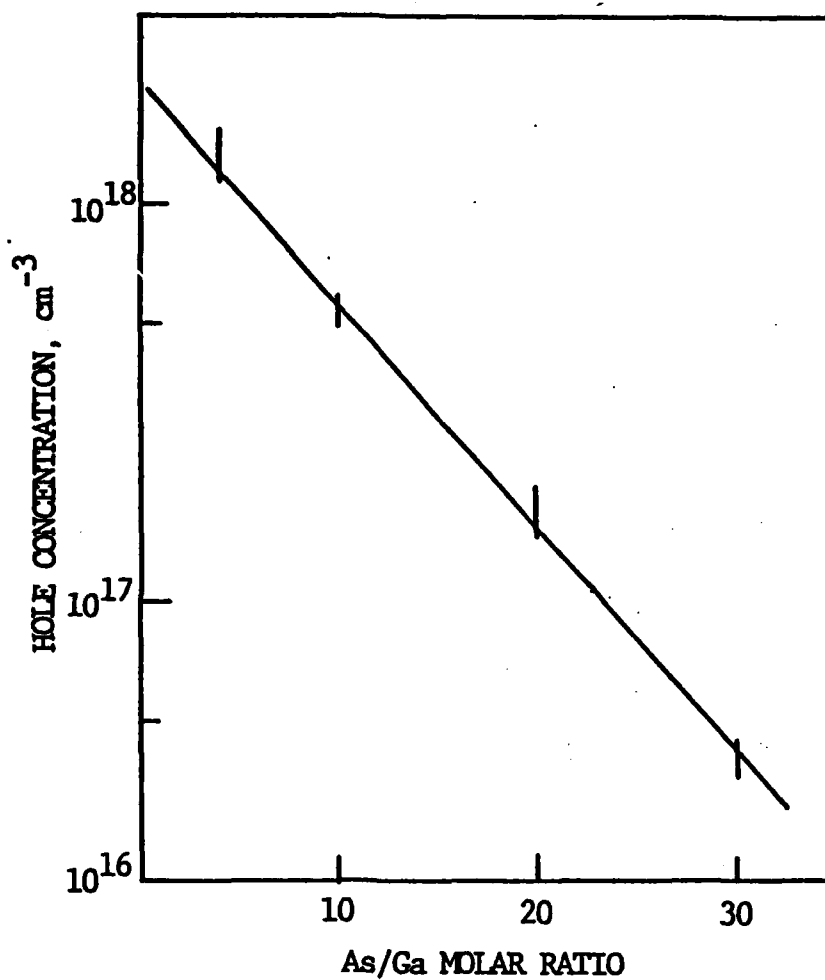


Figure 4. The hole concentration in the epitaxial GaAs films as a function of AsH_3 /TMG molar ratio. The deposition conditions: deposition temperature, 500°C ; mole fraction of TMG, 1.6×10^{-4} ; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.

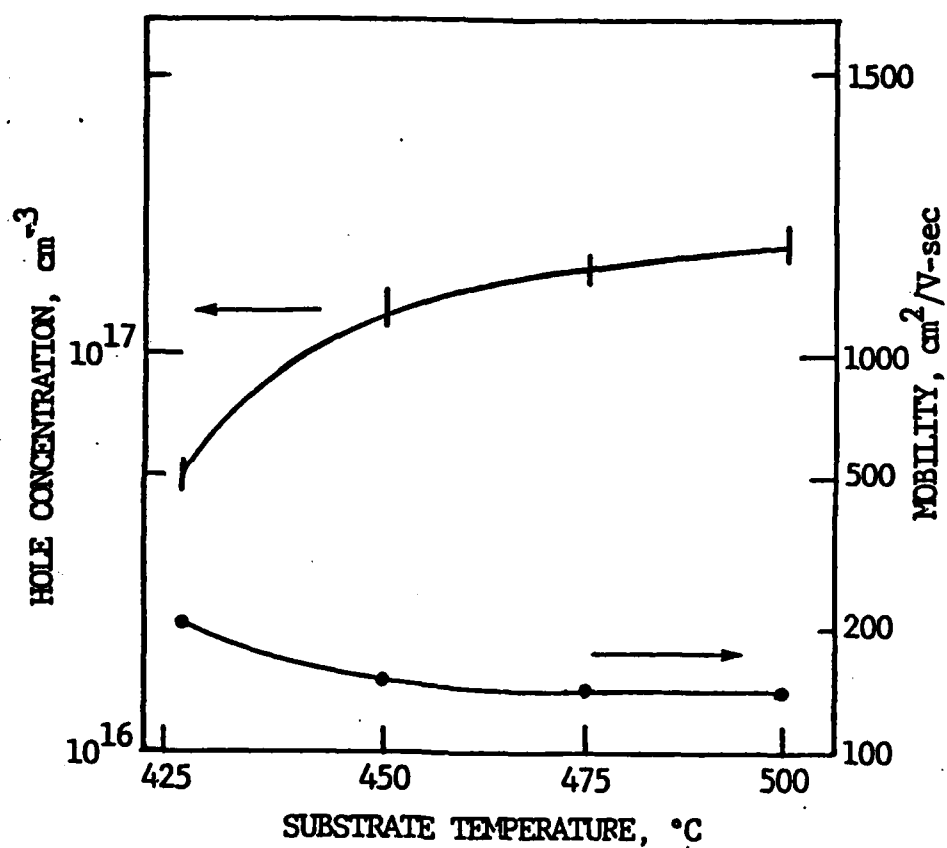


Figure 5. The hole concentration and mobility in the epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 2.

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